

POTENTIAL UTILIZATION OF NATURAL ZEOLITES FOR TREATING COALBED NATURAL GAS (CBNG) PRODUCED WATERS STUDIES¹

George F. Vance², Hongting Zhao, Michael A. Urynowicz, Girisha K. Ganjegunte, and Robert W. Gregory

Abstract: Fast development of the coalbed natural gas (CBNG) industry in many parts of the western U.S. has resulted in the co-production of potentially saline-sodic waters, hereafter referred to as CBNG water. Management of CBNG water is a major environmental challenge because of its quantity and quality. In this study, the potential utilization of calcium (Ca²⁺)-rich natural zeolites were examined for removal of sodium (Na⁺) from CBNG waters. Zeolite samples examined were from the St. Cloud (ST) zeolite mine in Winston, NM and the Bear River (BR) zeolite mine in Preston, ID. The zeolite materials were used in adsorption kinetic/isotherm studies and column experiments. A surrogate CBNG water that simulated the water chemistry of CBNG waters was used in the various studies described herein. Results indicated that a Langmuir model fit the adsorption data well. The maximum adsorption capacities from the adsorption isotherms for ST-Zeolite and BR-Zeolite were 9.6 and 12.3 (mg/g), respectively, accounting for approximately 38% and 39% of their measured CEC values. Column studies indicated that a metric tonne (1000 kg) of ST-zeolite and BR-zeolite can be used to treat 16,000 and 60,000 liters of CBNG water, respectively, in order to lower the sodium adsorption ratio (SAR, mmol^{1/2} L^{-1/2}) of the simulated CBNG water from 30 mmol^{1/2} L^{-1/2} to an acceptable level of 10 mmol^{1/2} L^{-1/2}. Based on the results of this study Na⁺ removal with zeolite appears to be a cost-effective water treatment technology for maximizing the beneficial use of poor-quality CBNG water. Ongoing studies are evaluating water treatment techniques involving the direct application of zeolite to CBNG waters and development of a field scale prototype.

Additional Keywords: Zeolite, Adsorption, Coalbed Methane Produced Water, Clinoptilolite, Langmuir, Powder River Basin, Sodium Adsorption ratio, SAR.

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Introduction

Coalbed natural gas (CBNG) development in the Powder River Basin (PRB) of Wyoming and Montana has increased dramatically in the past 10 years, resulting in the generation of a significant energy resource as well as a number of serious environmental and regulatory questions. A contentious issue associated with CBNG production is what to do with all the produced water that must be removed in order for coal seams to degas. The primary concern with CBNG produced waters is their high sodium adsorption ratios (SAR) and the influence the sodium (Na^+) has on soils, vegetation, wildlife and livestock in different environments, e.g., streams, agricultural lands, rangelands, and other PRB ecosystems (Ganjugunte *et al.*, 2005; Vance, 2006). Some CBNG producers are treating poor-quality CBNG water using ion exchange, reverse osmosis, and other similar types of treatment to improve its quality for release into streams and other waterways, or for beneficial purposes such as irrigation. Unfortunately, the current CBNG-water treatment technologies are often very expensive (Vance *et al.*, 2004, 2006). The purpose of this study was aimed to develop a cost-effective treatment technology by exploring the potential application of calcium (Ca^{2+})-rich zeolitic materials as Na^+ exchangers. Reduction in the amount of Na^+ and a lowering of the SAR levels will result in CBNG waters that can be beneficially used by the industry, land owners, and for downstream users.

Natural zeolites exhibit distinctive cation exchange capacity (CEC) and adsorption properties, and have been effectively utilized to remove toxic elements from polluted waters (Barrer, 1978; Mumpton, 1999; Gunter and Zanetti, 2000; Bowman, 2003; Wingenfelder *et al.*, 2005). Different zeolites have cation preferences that result in cation selectivity. Clinoptilolite and chabazite zeolites have a preference for larger cations. For example, clinoptilolite cation selectivity follows the order of: $\text{Cs} > \text{Rb} > \text{K} > \text{NH}_4 > \text{Ba} > \text{Sr} > \text{Na} > \text{Ca} > \text{Fe} > \text{Al} > \text{Mg} > \text{Li}$, whereas chabazite selectivity is $\text{Tl} > \text{Cs} > \text{K} > \text{Ag} > \text{Rb} > \text{NH}_4 > \text{Pb} > \text{Na} = \text{Ba} > \text{Sr} > \text{Ca} > \text{Li}$ (Mumpton, 1999). The slightly higher preference of Na^+ over Ca^{2+} of clinoptilolite zeolites makes them a better choice for removing Na^+ from CBNG waters. Some of the advantages of utilizing natural zeolite as a cation exchanger for CBNG water treatment are the large number of deposits throughout the western U.S., low mining cost, and their capacity to retain natural and anthropogenic cations. A bench scale study was thus conducted to evaluate the applicability of natural zeolites for development of a cost-effective treatment system for removing Na^+ from CBNG waters.

Experimental Section

Materials

Two commercially available clinoptilolite zeolite samples obtained from the St. Cloud (ST) zeolite mine in Winslow, NM and the Bear River (BR) zeolite mine in Preston, ID were used in this study. Exchange cations and CEC for the zeolites are listed in Table 1.

Table 1. Exchangeable cations (meq/100 g) and CEC (meq/100 g) of the zeolites studied.

Sample	Designation	Na^+	Ca^{2+}	Mg^{2+}	K^+	CEC
Zeolite-Clinoptilolite (St. Cloud, NM)	ST-Zeolite	4	77	18	13	112
Zeolite-Clinoptilolite (Bear River, ID)	BR-Zeolite	10	67	3	56	136

The water chemistry of the surrogate CBNG water (Table 2) was chosen by compiling published data from various sources (BLM, 2003; King *et al.*, 2004) and prepared using appropriate amounts of inorganic chemicals and tetraethyl orthosilicate as the silicon (Si) source.

Table 2. Water Chemistry of the Synthetic CBNG Water (mg/L).

Element	Na	Ca	Mg	K	Cl	SO ₄	HCO ₃	SiO ₂	SAR	pH
Concentration	411	10	2.5	2.5	65.8	10	1010	10	30.1	8.90

Methods

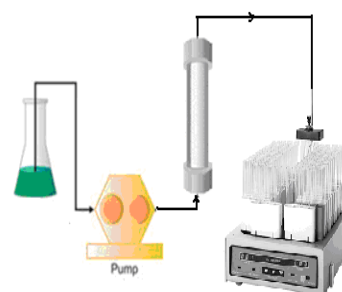
Zeolite exchangeable cation concentrations and cation exchange capacities (CEC) were determined by a modified method of Cerri *et al.* (2002). Briefly, 1.0 g of zeolite sample was reacted for 2 hours with 33 ml of 1 M ammonium acetate (NH₄Ac) at room temperature followed by centrifugation and filtration (Whatman filter #42) of the supernatant. This process was repeated two more times with the three extracts combined in a volumetric flask that was brought to total volume of 100 ml using 1 M NH₄Ac.

The adsorption kinetics study was carried out using 20.0 g zeolite samples diluted with the surrogate CBNG water to 1000 ml at ambient temperature. Aliquots of these samples (~5 ml) were collected at various times using a syringe with a GHP Acrodisc 0.2 µm filter attached. The samples were then acidified using concentrated nitric acid (HNO₃) and stored until analyzed.

Adsorption isotherms were conducted using the batch equilibration technique (Zhao, *et al.*, 2004). A 5.0 g zeolite sample was weighed into 50 ml polyethylene bottles containing varying amounts of NaCl. The tubes were then filled with 45 ml of sodium bicarbonate (NaHCO₃) solution with a concentration of 1010 mg/L as HCO₃⁻. The initial Na⁺ concentrations in the tubes ranged from 0 to 8,400 mg/L. The tubes were shaken on a reciprocal shaker for 48 hours, centrifuged and the supernatant solution filtered and acidified as described above.

A continuous flow-through column apparatus was utilized in order to predict zeolite performance under practical treatment system conditions. The basic column parameters were as follows: weight of zeolite: 132.0 g; column diameter: 25.0 mm; column length: 250 mm (for ST-zeolite); 260 mm (for BR-zeolite); flow rate: 3.0 ml/min; bed volume: ~125 cm³. The effluents were collected using an automatic fraction collector.

The concentrations of cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) in solution were analyzed using Inductively Coupled Plasma (ICP) spectrophotometry. The solutions were also measured for pH using pH meters.



Results and Discussion

Zeolite Characterization

The X-ray diffraction (XRD) examination indicated a significant occurrence of clinoptilolite in both ST-zeolite and BR-zeolite samples (80% and 85% clinoptilolite according to manufacturer's specifications). Other minerals identified by XRD analysis included smectite,

quartz, cristobalite, feldspar, and illite. The reported rock analytical data using X-ray fluorescence (XRF) spectrometry for ST-zeolite are: SiO₂ (57.8-68.2%), Al₂O₃ (11.6-14.0%), TiO₂ (0.2-0.6%), Fe₂O₃ (1.21-3.71%), MnO (0.04-0.06%), CaO (2.71-6.10%); Na₂O (0.25-0.84%), K₂O (2.38-3.24%), P₂O₅ (0.02-0.19%) and loss on ignition values (LOI) (10.3-12.1%). A chemical analysis of the BR-zeolite suggests a composition of SiO₂ (67.4%), Al₂O₃ (10.6%), TiO₂ (0.27%), Fe₂O₃ (1.7%), MnO (<0.01%), CaO (2.23%), Na₂O (0.59%), K₂O (4.19%), P₂O₅ (0.10%), MgO (0.45%) and LOI (11.4%). Measured CECs were 112 and 136 meq/100g for ST-zeolite and BR-zeolite, respectively. As shown, both ST-zeolite and BR-zeolite samples are naturally enriched with exchangeable Ca²⁺. It is interesting to note that BR-zeolite contains considerable exchangeable K⁺ (56 meq/100g) as compared to that of ST-zeolite (13 meq/100g).

Adsorption Kinetic and Isotherm

Figure 1 indicates that Na⁺ adsorption rates are faster for BR-zeolite when compared to ST-zeolite. In addition, BR-zeolite removed more Na⁺ and released greater amounts of Ca²⁺ than that of ST-zeolite. Other major exchangeable cations (i.e., K⁺ and/or Mg²⁺) can also be replaced by Na⁺ in short term experiments (Fig. 1). The adsorption kinetics is related to many factors including particle size, pore structure, and solute diffusion.

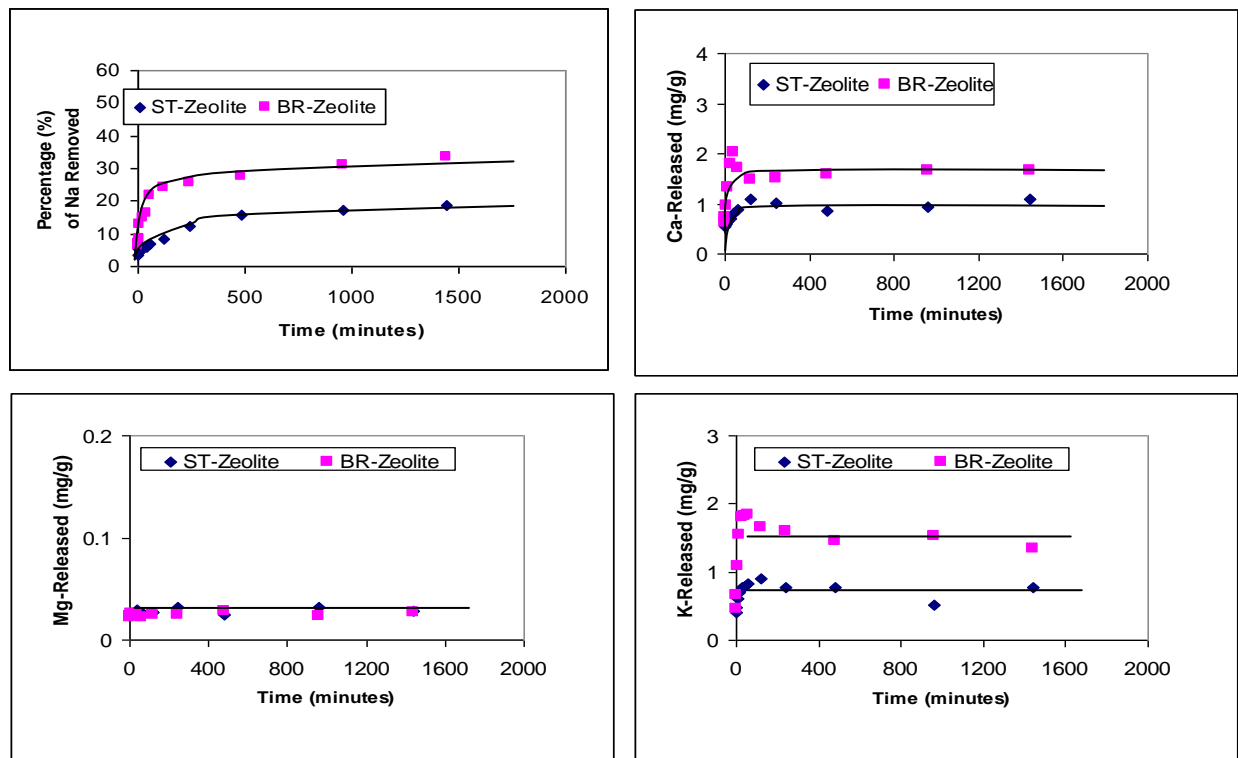


Figure 1. Na⁺ adsorption and Ca²⁺, Mg²⁺ and K⁺ release kinetics for ST-zeolite and BR-zeolite

The Na⁺ isotherm curves showed L-type adsorption on ST-zeolite and BR-zeolite (Fig. 2). The L-type isotherms are described well using the Langmuir equation:

$$q = q_{\max} K C / (1 + K C) \quad [\text{Eq. 1}]$$

where q is the amount adsorbed (mg/g), q_{max} is the maximum adsorption capacity of the solid

phase, K is the Langmuir constant, and C is the equilibrium Na^+ aqueous concentration.

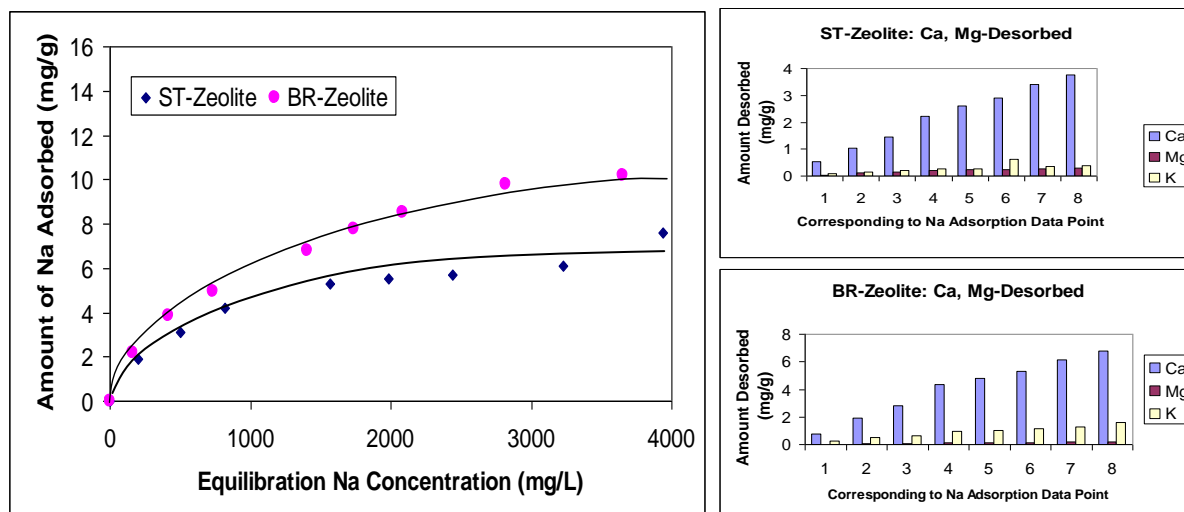


Figure 2. Na^+ adsorption isotherms and corresponding Ca^{2+} , Mg^{2+} and K^+ release from ST-zeolite and BR-zeolite

The BR-zeolite had a greater adsorption affinity for Na^+ than did the ST-zeolite at the same equilibrium solution Na^+ concentrations. The maximum Na^+ adsorption capacities from the isotherms (Fig. 2 and Table 3) for ST-zeolite and BR-zeolite are 9.6 and 12.3 (mg/g) or 0.42 and 0.54 (meq/g), which accounts for approximately 38% and 39% of their measured CEC values, respectively. The previously reported cation selectivity order indicated Na^+ is only slightly preferred over Ca^{2+} on clinoptilolite, while K^+ is more strongly adsorbed. The binding strength constant (K) of BR-zeolite is higher than that of ST-zeolite, indicating that Na^+ could be more strongly adsorbed by BR-zeolite. The adsorption isotherm results are consistent with the findings observed in the kinetic study.

Table 3. Langmuir adsorption parameters for the adsorption of Na^+ by ST-zeolite and BR-zeolite

Sample	q_{\max} (mg/g)	K	R^2
ST-Zeolite	9.6	872	0.965
BR-Zeolite	12.3	1053	0.983

Cation adsorption behaviors (i.e., adsorption capacity and selectivity) by zeolites are related to a variety of factors such as mineral purity, crystallinity, media purity, cation valence/hydration degree and pre-existing cations and multiple adsorption sites with varying degree of accessibility as well as rate-limiting steps (mass transfer and diffusion) (Zhao *et al.*, 2004). Although ST-zeolite contains a slightly higher exchangeable Ca^{2+} than that of BR-zeolite, the ease of which the Ca^{2+} exchanged from ST-zeolite is lower than that of the BR-zeolite, suggesting that the Ca^{2+} in ST-zeolite may occupy the more strongly adsorbed sites. The higher K^+ in BR-zeolite suggest that it could occupy the more strongly adsorbed sites thus leaving the Ca^{2+} in relatively weakly adsorbed sites making the Ca^{2+} in BR-zeolite more easily replaced by Na^+ than that in ST-Zeolite. Overall, the adsorption results of this study suggest that both zeolites can be used to reduce the Na^+ level in CBNG waters by releasing K^+ , Ca^{2+} , and Mg^{2+} , with the BR-zeolite

having a higher adsorption capability than that of ST-zeolite.

Considering charge balance, the amount of Ca^{2+} , Mg^{2+} and K^+ released accounted for more than 85% of the adsorbed Na^+ on both ST-zeolite and BR-zeolite, which suggests that the difference is probably due to the release of other cations. Longer term experiments may provide better evidence for the removal of Na^+ from CBNG waters.

Column Study

Results from the zeolite column studies are shown in Fig. 3. The column performance results are consistent with the tendency observed in the batch adsorption kinetic/isotherm studies. Monitoring of the effluent solution pH indicated that, as compared to that of the influent solution ($\text{pH} = 8.90 \pm 0.10$), there was no significant change in pH values of the leachates for ST-zeolite ($\text{pH} = 9.00 \pm 0.30$) and for BR-zeolite ($\text{pH} = 8.90 \pm 0.10$). We found that BR-zeolite could remove more Na^+ from the synthetic CBNG waters and that there was a longer breakthrough period for the BR-zeolite compared to the ST-zeolite. It is interesting to note that, for BR-zeolite, significant K^+ was also released which is an important plant nutrient.

If one considers CBNG water with SAR values equal to or less than 10 to be suitable for land application, from the SAR breakthrough curve (Fig. 3), it could be estimated that, in a flow-through treatment system until the effluent SAR was 10 $\text{mmol}^{1/2} \text{L}^{-1/2}$, the amount of the synthetic CBNG water ($\text{SAR} = 30 \text{ mmol}^{1/2} \text{L}^{-1/2}$) that can be treated per metric tonne (1,000 kg) of ST-zeolite and BR-zeolite would be about 8,000 and 30,000 L, respectively.

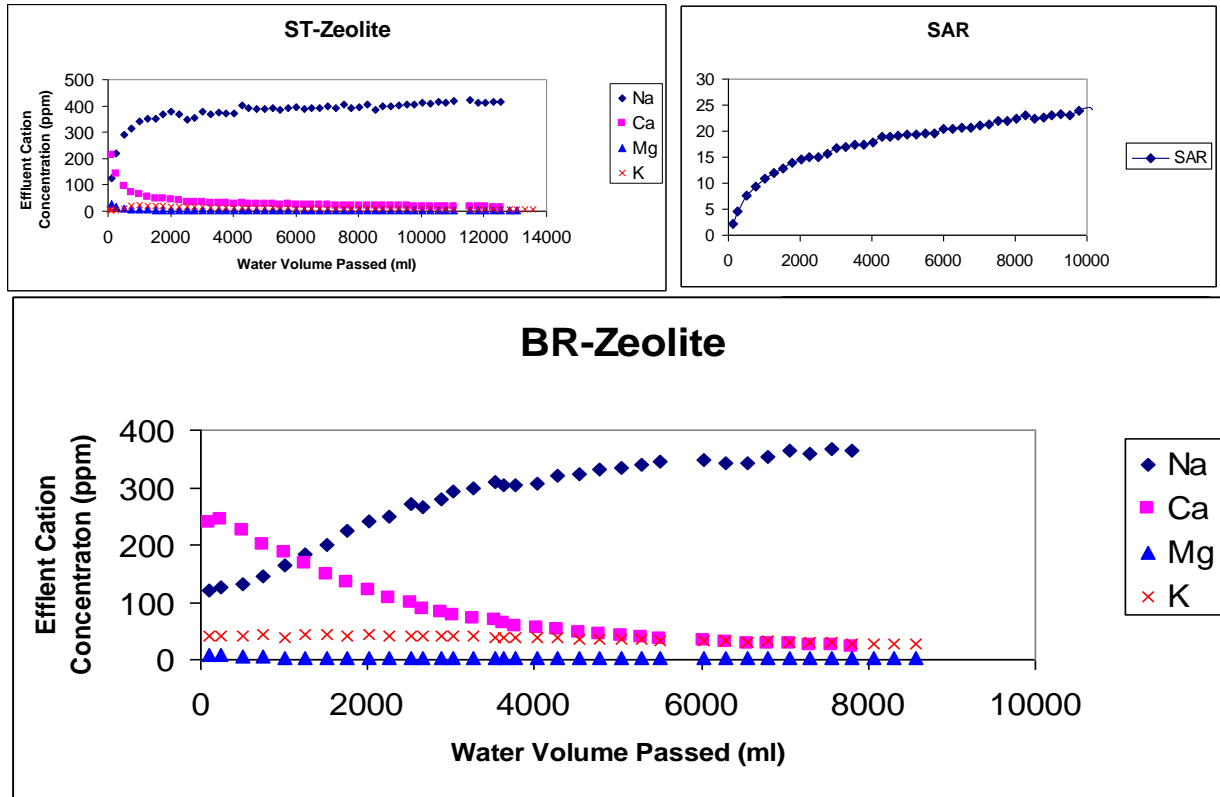


Figure 3. Column breakthrough curves for ST-zeolite and BR-zeolite

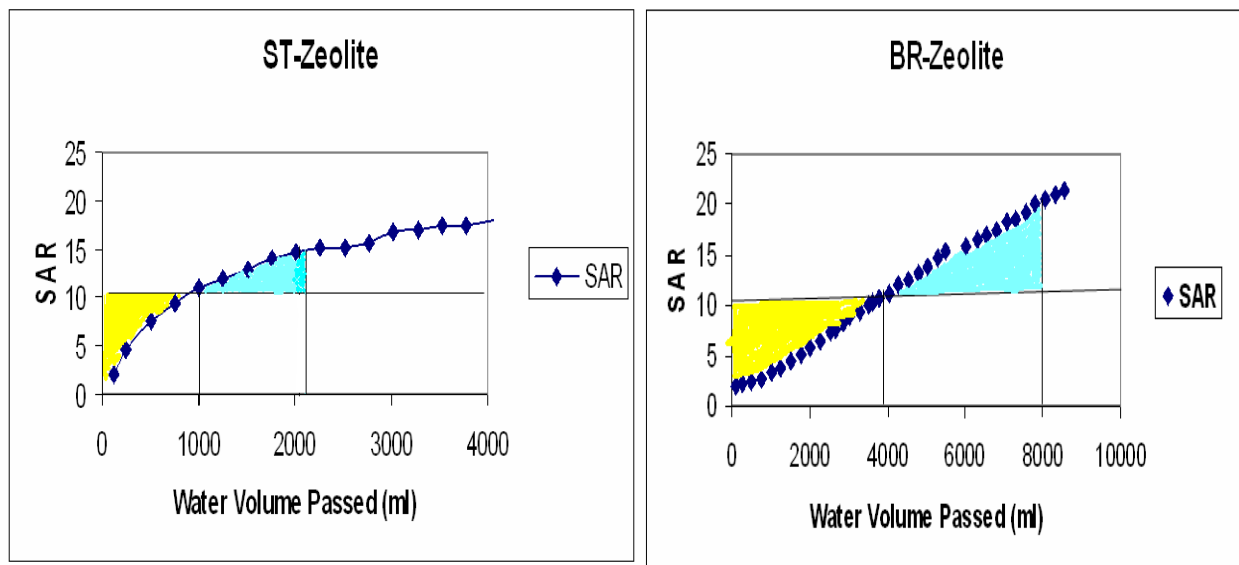


Figure 4. Cumulative estimation of treatable water volume by ST-zeolite and BR-zeolite

On the other hand, if CBNG water were treated and collected in a large containment reservoir, CNBG waters processed initially would have very low SAR values. By integrating the area between the SAR curve and $\text{SAR} = 10 \text{ mmol}^{1/2} \text{ L}^{-1/2}$ cutoff line (Yellow area in Fig. 4), the amount of additional CNBG waters that can be treated and combined with the initially processed waters to reach a final SAR value of $10 \text{ mmol}^{1/2} \text{ L}^{-1/2}$ can be estimated. Extrapolating the results suggest that one metric ton (1,000 kg) of ST-zeolite and BR-zeolite can treat approximately 16,000 and 60,000 L of the synthetic CBNG water ($\text{SAR} = 30 \text{ mmol}^{1/2} \text{ L}^{-1/2}$), respectively, to a final SAR around $10 \text{ mmol}^{1/2} \text{ L}^{-1/2}$, which is considered safe for land application for agricultural use.

Results from the column studies will be useful for designing a scaled-up pilot project for future applications. Column performance depends upon a variety of factors that include adsorbent type, particle size, adsorption capacity, column diameter, water flow rate, adsorbent bed depth, weight of adsorbent in column, and contact time as well as water chemistry, all of which will be evaluated in future studies.

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