FINAL REPORT

INNOVATIVE TECHNOLOGY DEVELOPMENT TO MAXIMIZE BENEFICIAL USE OF PRODUCED WATER FROM COALBED NATURAL GAS OPERATIONS IN THE POWDER RIVER BASIN, WYOMING

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ABSTRACT

Wyoming has experienced rapid growth in the development of its coalbed natural gas (CBNG), resources. One of the most contentious issues surrounding CBNG production is how to deal with the co-produced water that must be removed to allow coal seams to degas? A Wyoming CBNG task force has been formed to investigate alternative uses of water produced during CBNG production. One area of interest has been the beneficial use of CBNG co-produced waters in order to enhance gas production and environmental sustainability. The primary concern with CBNG produced waters is the amount and influence sodium (Na^+) (as defined by the sodium adsorption ratio (SAR)) has on soils, vegetation, wildlife and livestock in different environments, e.g., streams, agricultural lands, rangelands, and other ecosystems. We have researched the development of a water treatment system based on cation exchange between natural zeolites and CBNG waters. Research indicates that there is a significant reduction in the amount of Na^+ and a lowering of SAR in CBNG produced waters after these waters are processed with the zeolitic materials. Our research included three primary tasks: 1) determination of cation exchange capacity (CEC), exchangeable cations, and opportunities of selected zeolites deposits; 2) evaluation of cation exchange reactions between CBNG produced water and natural zeolites to reduce CBNG water SAR's; and 3) design of a water treatment scenario based on cation exchange between natural zeolites and CBNG produced waters. Studies on the exchange and kinetic reactions between CBNG waters and Ca-zeolites were conducted to formalize and quantify the exchange process. Industry, land owners, and downstream users will benefit from this new method of reducing Na^+ and lowering SARs of CBNG waters.

INTRODUCTION

Development of CBNG in the Powder River Basin (PRB) of Wyoming and Montana has increased dramatically in the past 10 years, resulting in significant CBNG production as well as many environmental and regulatory issues (Ayers 2002, McBeth *et al.* 2003, RIENR 2005). One of the issues involves the release of copious quantities of groundwater removed to recover the natural gas (King *et al.* 2004c, Vance *et al.* 2004, Vance 2006). Not only are the thick coal seams in the PRB rich in natural gas, they are also important regional aquifers (Wheaton and Olson 2001, Wheaton and Metesh 2002). In order to produce the absorbed natural gas from the coals, formation pressures must be reduced by removal of water. Existing data strongly suggests that CBNG activities in the PRB will expand west into deeper coals (Figure 1), that the quality of water from the coal will deteriorate, and that the volume of the water per well will increase significantly (BLM 2003). CBNG stakeholders in the PRB have focused on the disposal of the water. As a consequence a very contentious atmosphere has evolved around CBNG activities. Most of the contention surrounding CBNG water would be eliminated if a significant portion of the waters could be put to beneficial use (King *et al.* 2004c, Vance *et al.* 2004).
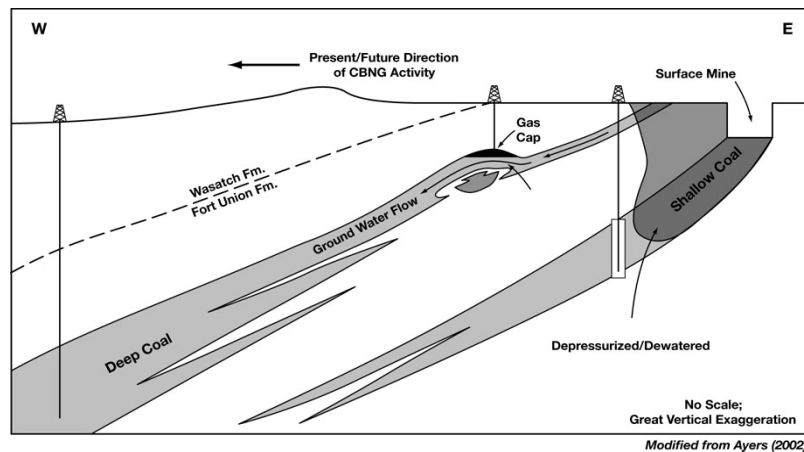

Figure 1. Early coal bed natural gas (CBNG) wells in the PRB were located in depressurized strata adjacent to surface mines around Gillette, WY. Presently CBNG activity is moving to the west and exploiting deeper and thicker coalbeds (i.e., Big George coalbed).

WDEQ's NPDES permits/enforcement and BLM's drilling permits take into consideration water management issues relating to CBNG activities. In addition, the WO&GCC's permitting and reclamation of off-channel reservoirs and the WSEO water rights issues also involve CBNG activities throughout Wyoming. Estimates suggest CBNG production from the relatively thick coal seams in the PRB will reach a peak of about 5.0 Bcf/d by 2008, which will require more than 25,000 wells. Clearly, these estimates are becoming reality, with the amount of both gas and CBNG water increasing at a rapid rate. The BLM's Environmental Impact Assessment (EIS) for the PRB had allowed unlined, off-channel reservoirs so the water can be disposed by evaporation and/or infiltration into the alluvium (BLM 2003). Estimates suggest only 2% of the water subjected to off-channel storage is available for beneficial use (i.e., livestock water). To many stakeholders in the arid PRB believe this "preferred" water disposal procedure is a waste of an important and valuable resource – water!

Water treatment is an important issue for maintaining the viability of the CBNG industry in the PRB and the rest of the western United States (Vance 2006). In the future, the CBNG industry will either improve water disposal options by developing new or improved technologies, or be faced with interminable litigation and delay. The most important aspect of the produced water from the deeper coals is the significant increase in the SAR. For comparison, water produced from shallow coals near Gillette, WY have SAR's ranging from 6 to 12, whereas the water produced from the deeper coals near Sheridan, WY have SAR's ranging from 45 to 60. In the eastern (i.e., shallow coals) portion of the PRB, discharge of CBNG produced water is limited to SARs of 10 or less for the northeastward flowing Belle Fourche and Cheyenne River drainages. For the northward flowing Powder River, the SAR default limit is 7. CBNG produced water significantly degrades to the north and west, particularly with respect to SAR, and the water quality requirements for the receiving streams become more stringent.

CBNG waters have been used as a source of irrigation water in the PRB (King *et al.* 2004a,b, Vance *et al.* 2004). Soils in PRB are dominated by smectitic clays, and nearly 41% of the PRB area is covered with soils characterized by poor drainage (BLM 2003, Ganjegunte *et al.* 2005). Application of CBNG waters with high SAR's can have negative impacts on soil physical and chemical properties (Ganjegunte *et al.* 2005). Irrigating soils with high SAR water can result in dispersion of soil clay particles and organic matter, resulting in surface crusting, reduced infiltration, and lower hydraulic conductivity, which could lead to poor vegetation growth (Vance and Stevens 2003, Ganjegunte *et al.* 2004). In order to avoid permanent damage to fragile PRB agricultural and rangeland ecosystems, it is necessary to reduce the Na^+ concentrations in the CBNG water so that it can be used safely for irrigation (i.e., crop production) or discharged to natural drainages (i.e., recreation and wildlife).

The technology researched in this project evaluated the use of natural zeolites as cation exchangers to achieve targeted SAR levels in CBNG produced waters. If this technology is utilized, a significant portion of CBNG water may be available for beneficial use (Vance *et al.* 2007). The University of Wyoming and Wyoming State Geological Survey will continue to pursue research that will evaluate a technology to treat CBNG produced water and improve its beneficial usage. The essential treatment is the removal of Na^+ from the produced water. With only Na^+ removal, most of the produced water could be used in some beneficial capacity. To accomplish this goal many technologies have been suggested (Rawn-Schatzinger *et al.* 2003). All of the suggested technologies have both promise and problems, but most importantly they are often too expensive. The solution to the problem is to find a practical, cost-effective and efficient method to treat the CBNG produced water in the PRB – not the best or ideal water management plan, but a practical water treatment technology that allows a significant portion of the CBNG produced water to be available for beneficial use.

Statement of Results and Benefits

The advantages of utilizing material from natural zeolite deposits as a cation exchanger in the treatment of PRB CBNG produced water are as follows: 1) zeolite deposits are at or near the surface and are easy to mine; 2) deposits are generally of large volume; 3) deposits commonly are flat-lying; and 4) deposits are often characterized by high mineral purity (>75%). Therefore the mining costs of the zeolite deposits are generally low (Mumpton, 1978, 2000). Typically the cost of mining and preparation (i.e., crushing and sizings) of zeolite for the end use application is minor with respect to transportation costs. Therefore, although accurate cost estimates for utilizing zeolite will not be possible until field experiments are completed, we conclude that

zeolite is probably the only large volume, low-cost, and easily disposable cation exchanger available.

The technology researched for resolving the problem of CBNG Na-rich waters is based on the use of natural clinoptilolite in cation exchange columns or beds to achieve targeted SAR levels in CBNG produced waters. The mineral name clinoptilolite as used in this project covers the heulandite-group zeolites. Typically the two end members of this group of zeolites, heulandite and clinoptilolite, are defined on the basis of thermal stability (i.e., heulandite being stable at higher temperatures than clinoptilolite). Ratterman and Surdam (1981) have demonstrated that with respect to thermal stability there exists a suite of intermediate members of the group. This demonstration is important to our research because the intermediate members have CaO/Na$_2$O ratios ranging from 0.4 to 4.9 (Sheppard and Gude, 1973). Moreover, Ratterman and Surdam (1981) showed that these intermediate zeolite-group members are found in many zeolite-rich deposits (i.e., altered tuffaceous deposits). A survey of the literature suggests that the intermediate members are common in the zeolite deposits (Sheppard and Gude, 1968, 1969, 1973; Surdam and Sheppard, 1978; Ratterman and Surdam, 1981). A major aspect of our research focused on the utilization of intermediate relatively Ca-rich clinoptilolites as the solid cation exchanger in the treatment of CBNG produced water. This will require material from a natural zeolite-rich deposit that is >75% clinoptilolite, is Ca-rich (i.e., Ca > Na) or that can be made Ca rich through Ca saturation, and has a cation exchange capacity (CEC) of 1.75 meq/gm or greater. These values are all within the range of parameters observed for natural clinoptilolite characteristics (Sameshima, 1978; Stonecipher, 1978; Kastner and Stonecipher, 1978; Iijima, 1978; Hay, 1995; Ogihara and Iijima, 1989).

Objectives

The primary objective of our research was to evaluate the development of a water treatment alternative that maximizes the beneficial use of CBNG produced water. In order to accomplish this objective, research was conducted according to three tasks that included:

Task 1.0 – Determine cation exchange capacities (CEC), exchangeable cations, and volumetrics of selected zeolite deposits,

Task 2.0 – Evaluation of the potential for cation exchange reactions between CBNG produced water and natural zeolite deposits to reduce CBNG water SAR's, and

Task 3.0 – Design an economic, viable water treatment scenario based on cation exchange between natural zeolite and CBNG produced waters.

MATERIALS AND METHODS

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. About 40 natural zeolites have been identified during the past 200 years, the most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite (Table 1). More than 150 zeolites have been synthesized, which are primarily zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

Natural zeolites exhibit distinctive CEC and adsorption properties, and have been effectively utilized to remove toxic elements from polluted waters (Barrer 1978, Collela 1996, Pansini 1996, Mumpton 1999, Duong *et al.* 2005, 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: Cs > Rb > K > NH$_4$ > Ba > Sr > Na > Ca > Fe > Al > Mg > Li, whereas chabazite selectivity is Tl > Cs > K > Ag > Rb > NH$_4$ > Pb > Na = Ba > Sr > Ca > Li (Mumpton, 1999, 2000). The slightly higher preference of Na$^+$ over Ca^{2+} of clinoptilolite zeolites makes them a better choice for removing Na$^+$ from CBNG waters (Table 1).
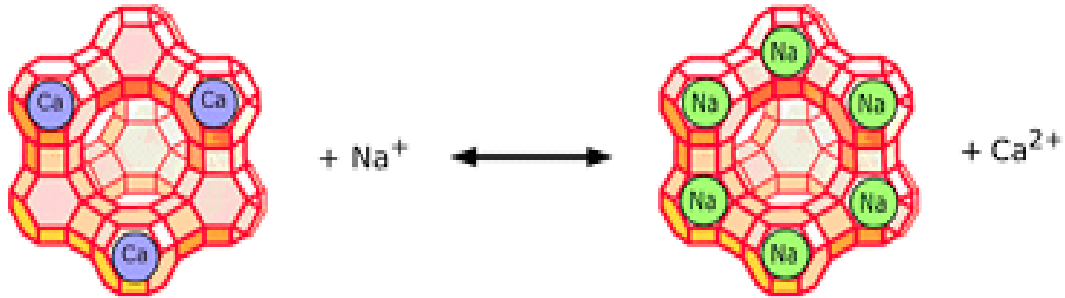

Table 1. Ideal cation exchange capacity of some natural zeolite: data calculated using the unit cell formula (Inglezakis 2005)

Zeolite	Cation Exchange Capacity (CEC) (meq/g)
Chabazite	3.84
Clinoptilolite	2.16
Erionite	3.12
Ferrierite	2.33
Heulandite	2.91
Laumontite	4.25
Mordenite	2.29
Phillipsite	3.31
Faujasite	3.39

Commercial zeolite deposits in the United States are associated with the alteration of volcanic tuffs in alkaline lake deposits and open hydrologic systems. Commercial deposits in the United States are in Arizona, California, Idaho, Nevada, New Mexico, Oregon, Texas, Utah, and Wyoming. Zeolites in these deposits are chabazite, clinoptilolite, erionite, mordenite, and phillipsite. Other components, such as orthoclase and plagioclase feldspars, montmorillonite, opal, quartz, and volcanic glass, are present in some deposits.

In 2002, nine companies mined natural zeolites in the United States. Two additional companies involved in zeolites during 2002 sold from stocks or purchased zeolites from other producers for resale. Chabazite was mined in Arizona and clinoptilolite was mined and processed in California, Idaho, Nevada, New Mexico, Oregon, Texas, and Wyoming. New Mexico produced the greatest amount of zeolite in 2002. Total domestic production of zeolites was estimated to be 46,000 metric tons (t) compared with an estimated 36,400 tonne in 2001.

Selection of Materials

Zeolite samples were collected from several deposits in Nevada, California, New Mexico, Idaho and Wyoming (Table 2). These sites were chosen based on reported chemical analysis and CEC of these zeolite deposits. Additionally, three of the sites are active zeolite mines (Ash Meadows, NV, Bear River, Idaho and St. Cloud, NM). Two sites are currently inactive but have been active in the recent past (Mud Hills, CA, and Fort La Clede, WY) and presumably could be reopened at minimal cost. Following are brief descriptions of the sample locations and their geologic setting, along with their CEC.

Table 2. Natural zeolite samples (Clinoptilolite-Dominant) obtained for this study

Sample	CEC (meq/g)	Source, location
AM1	1.60	Ash Meadows, Nye County, NV
FC1	1.36	Fossil Canyon, San Bernardino County, CA
FC2A	1.88	Fossil Canyon, San Bernardino County, CA
FC2B	1.96	Fossil Canyon, San Bernardino County, CA
MH1	1.71	Mud Hills, San Bernardino County, CA
SC1	0.62	St. Cloud, Sierra County, NM
BRZ1a	1.29	Bear River, Franklin County, ID
BRZ1b	1.21	Bear River, Franklin County, ID
FL1a	1.92	Fort LaClede, Sweetwater County, WY
FL1b	2.15	Fort LaClede, Sweetwater County, WY

Extensive research was carried out in an effort to identify target locations with favorable mineralogy, chemistry, and sufficient volume to sustain a mining operation capable of supplying enough material for water treatment described herein. Zeolite beds should be of sufficient thickness (several meters or more), laterally extensive with minimal dip and should also be covered by a minimum of overburden.

Following are brief descriptions of the most promising sample locations and their geologic setting and history, along with mention of the chemistry and CEC of the samples. CEC determinations were performed by Dr. Steve Boese of the UW Department of Geology and Geophysics. Other information sources are as noted. See Tables 1 and 2 for CEC.

The Ash Meadows zeolite deposit is located in Amargosa Valley, Along the California-Nevada border between Las Vegas and the Death Valley area of California. The zeolite is situated in a gently dipping sequence of altered lacustrine deposits in Inyo County, CA and extends in to Nye County, NV. The deposits are believed to have originated as late Tertiary tuffaceous (Pleistocene) ash fall deposits that settled into a large lake referred to as Lake Tecopa (Sheppard and Gude, 1968). The vitric material in the ash fall deposits was later altered and zeolitized by reactions between the siliceous matrix of the ash with the saline-alkaline waters of the lake and, to some extent meteoric waters (Sheppard and Gude, 1968). The zeolite mined at Ash Meadows has a CEC value of 1.60 meq/g with major cation weight percentages of 3.73% K_2O, 3.47% Na_2O, and 0.97% CaO.

Approximately 160 km to the southwest of Ash Meadows is the Mud Hills area containing zeolites in the Barstow Formation of Miocene age. This formation contains lacustrine and fluvial deposits with tuff making up approximately 2% of the stratigraphic section. As is thought to be the case with the Ash Meadows zeolites, the zeolites in the Barstow formation are believed to have formed by diagenetic reactions between the vitric material in the tuff with the lake waters and to some extent, connate waters ((Sheppard and Gude 1969). The tuff beds range in thickness from 0.3 to >2 m (Sheppard and Gude 1969). We collected samples from the area of the inactive Mud Hills zeolite mine and also in the Fossil Canyon area to the west of the Mud Hills mine approximately 8 km. The CEC value of the Mud Hills sample is 1.71 meq/g. with major cation values of 1.63% K_2O, 3.57% Na_2O, and 1.41% CaO. Fossil Canyon was also of interest because of its high Ca content of 2.25 wt% (Shepard and Gude 1969). CEC values for the Fossil Canyon zeolite samples range from 1.88 – 1.96 meq/g. Major cation weight percentages are 1.63% K_2O, 3.57% Na_2O, and 1.41% CaO.

Samples were also collected from the St. Cloud zeolite mine near Winston, NM. The St. Cloud zeolite deposit is located approximately 6 km south of Winston, NM within the Winston graben. The Oligocene-Miocene Little Mineral Creek tuff, which is a rhyolitic ash flow, hosts the commercial grade clinoptilolite. This ash flow is overlain by the unconsolidated conglomerates of the Santa Fe formation (Austin and Bowman 2002). Diagenesis of the ash flow deposits in an environment favorable to high silicon activity, i.e., a saline alkaline lake but with some apparent ground water influence (Pat Freeman, personal communication) resulted in the clinoptilolite beds.

The St. Cloud zeolite deposit crops out along nearly 2.5 miles of strike, and extends laterally in zones ranging from approximately 250-500 m (Austin and Bowman 2002). The zeolite is white to buff in color, with very homogenous and continuous beds up to 7.5 m thick where it is mined. Estimated reserves are 16 Mt (St. Cloud Zeolite website, accessed February 22, 2007, White *et al.* 1996).

The chemistry of the mined zeolite at St. Cloud is relatively high in Ca, at 2.71 – 6.1 (Austin and Bowman 2002) but with a slightly lower CEC of 0.62 meq/g. The mined zeolite product at St. Cloud contains 74 wt % clinoptilolite (Austin and Bowman 2002). Major cation weight percentages are 3.44% K_2O, 0.44% Na_2O, and 2.87% CaO.

At the Bear River zeolite mine, located just a few km northeast of Preston, outcrops of the Pliocene Cache Valley Formation of the Salt Lake Group host a major zeolite deposit. This region is found in the SE corner of the Riverdale 1:24,000 USGS quadrangle. Bear River Zeolite has controlled the deposit since 2001 and is actively expanding operations with new processing equipment. Most of their zeolite is sold for animal feed, air and water filtration, and as pozzolan, a material added to Portland cement to increase the long-term strength of concrete (Janotka *et al.* 2003). Much of their market is currently foreign, with common shipments to Peru, the Dominican Republic, Europe, and Canada.

The Bear River deposit crops out over a relatively large area (several km^2) consisting of numerous large hills. Beds are very homogenous and continuous with a total thickness of approximately 200 m) in some instances. The zeolite is colored a light, pastel gray-green due to iron impurities. The weathered surface is rusty to buff in color, and in most cases the deposit is covered with 3-5 m of soil. This soil has been found to be extremely fertile due to the ammonium-fixating properties of the zeolite. There is commonly good zeolite exposure on the hilltops, and estimated reserves are at 175 to 625 million tonne (Mt) (Lawrence, 2007, personal communication).

Samples collected from the quarry wall by the WSGS and Bear River Zeolite confirm a purity of 85-92% clinoptilolite with a balance of chalcedony. The chalcedony occurs in centimeter-scale dark green bands within the zeolite, lowering the CEC in localized areas due to the higher concentration of silica. Bear River Zeolite has also identified areas of variable CEC within the zeolite beds themselves. These zeolites are classified as potassic. Major cation weight percentages are 4.32% K_2O, 0.49% Na_2O, and 2.33% CaO. CEC is 1.25 meq/gram.

The Fort LaClede zeolite deposit occurs in the vicinity of and includes the robins egg blue tuff bed, part of the Eocene Adobe Town Member in the Washakie Formation (King and Harris, 2002). The robins egg blue tuff bed is a prominent marker bed visible for several km from historic Fort LaClede, trending northeast just southeast of Iron Pipe Draw at approximately the 2140 m elevation contour. This region is covered by the Fort LaClede, Fort LaClede NE, Kinney Spring, and Manual Gap 1:24,000 USGS topographic quadrangles, and the Kinney Rim 1:100,000 USGS topographic map. Land ownership in this area is a checkerboard of private and BLM sections. This deposit is currently controlled at least in part by U.S. Zeolites, although they have ceased production and the quarry appears to be abandoned as of this writing. The quarry is located in T16N, R98W, sec. 1.

The Adobe Town Member tuff is fairly resistant and ranges in color from a pastel robins egg blue to almost white. The beds in this area are nearly completely altered to clinoptilolite, forming zones several cm to 3.7 m thick. The zone of highest purity clinoptilolite is restricted to approximately 1.2 m and is easily recognized in the wall of the quarry pit. This deposit has been estimated to contain several million tonne of high grade material (Curry and Santini, 1986).

Samples were collected from the southwest area of the quarry pit, and to the west from undisturbed outcrop just over the ridge formed by the pit wall. Both the robins egg blue and the white colored tuffs of the Adobe Town Member were sampled and found to be approximately 90% clinoptilolite with very minor heulandite. These zeolites are classified as sodic. Major cation weight percentages are 1.53% K, 4.40% Na, and 1.50% Ca. CEC is 2.04 meq/gram.

Zeolite samples were also collected from southeast Fremont County, WY (King and Harris 2002). The Green Cove area of Beaver Rim is in sections 3 and 10 of T30N R96W. The samples were collected from two tuffaceous beds 1-2 m thick near the former US highway 287. These beds occur in Unit 3 of sequences within the middle-upper Eocene Wagon Bed Formation described by Van Houten (1964). The tuff beds in the Green Cove area appear extensive and are overlain by varying thicknesses of uneroded Unit 3 as well as Units 4 and 5 at the flanks of the cove. Van Houten (1964) describes "yellowish-orange to yellowish-gray and light gray limonite-stained, well sorted fine-grained altered biotitic vitric tuffs containing quartz and feldspar grains…" Iron staining appears unrelated to zeolitization, which was confirmed by our investigation as well. XRD analyses confirm strong clinoptilolite content in the samples collected. Cation exchange capacity and exchangeable cation analyses are pending as of this writing.

For the Ca-rich Arizona zeolite (CABSORB ZS500RW) used in this study, a chemical analysis of the zeolite suggests a composition of SiO_2 (69.5%), Al_2O_3 (16.6%), TiO_2 (0.47%), Fe_2O_3 (4.33%), CaO (4.49%), Na_2O (2.40%), K_2O (1.32%) and MgO (0.89%). This product was a partially upgraded chabazite. It originated from the high Na chabazite in the Grace pit and has somewhat different thermal treatments ranging from none to high temperature activation and different upgrading ranging from none to a partial recrystallization.

MATERIALS AND METHODS

X-ray Diffraction Analysis

X-ray analysis was conducted on the zeolites collected (Fig. 2 and Appendix). Samples were dried at approximately 80°C for several hours, which resulted in water loss ranging from <1% to >6%. Pulverized samples were scanned from 2-30° 2θ using Cu Kα radiation at 1.54 Å. The fewer peaks other than those of clinoptilolite in the samples suggest a higher percentage of zeolite. Typical impurities may include quartz, feldspars and/or clay minerals. Total chemical analyses were carried out on all the zeolite samples collected and are listed in the Appendix.
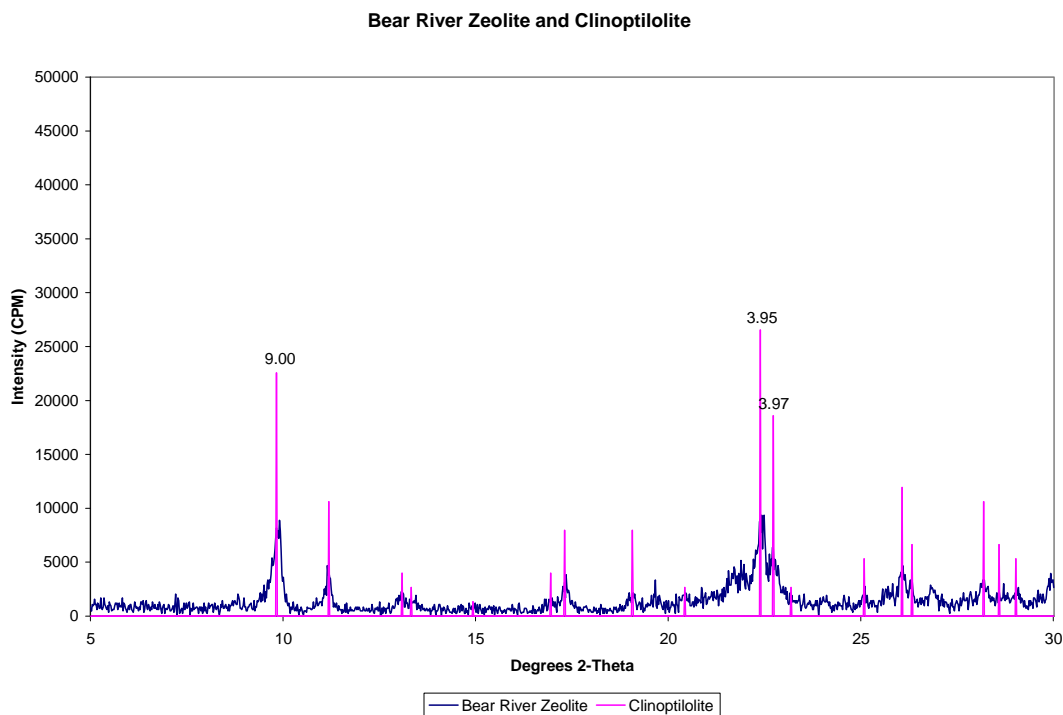
Bear River Zeolite and Clinoptilolite

Figure 2. Representative X-Ray Diffraction Patterns (Bear River Zeolite)

Cation Exchange Capacity and Exchangeable Cation determinations

Zeolite cation exchange capacities (CEC) and exchangeable cation concentrations were determined by a modified method of Cerri *et al.* (2002) (Table 3). For CEC measurements, the zeolites were first saturated with Na^+ that was displaced by a $(NH_4)_2SO_4$ solution to exchange NH_4^+ for Na^+. Exchangeable cations were determined using 1.0 g of zeolite sample that was reacted for 2 hours with 33 ml of 1 M ammonium acetate (NH_4Ac) 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 NH_4Ac. Following the displacement of exchangeable cations from the sample with NH_4^+ acetate, Na^+, K^+, Ca^{2+} and Mg^{2+} were analyzed following the inductively coupled plasma spectrometry (Suarez 1999).

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Table 3. Effective CEC and exchangeable cations (cmol kg⁻¹) of the different natural zeolite samples studied (Clinoptilolite-Dominant).

Sample	Location	Na^+	Ca^{2+}	Mg^{2+}	K^+	Effective CEC
Ash Meadows (AM)	Nevada	114	20	2	95	230
Fossil Canyon (FC1)	California	86	13	2	27	128
Fossil Canyon (FC2a)	California	149	13	1	35	198
Fossil Canyon (FC2b)	California	142	19	2	30	193
St. Cloud (SC)	New Mexico	3	61	17	7	87
Mud Hills (MH)	California	92	41	3	25	162
Bar River (BR)	Idaho	10	67	3	56	136
Fort LaClede (FL)	Wyoming	140	50	2	26	212

Adsorption Kinetics and Isotherms

Adsorption kinetics studies were carried out using 20.0 g zeolite samples diluted with surrogate CBNG water (Table 4) to 1,000 ml at ambient temperature. Aliquots of these samples (~5ml) were collected at various times using a syringe with a GHP Acrodisc 0.2 μm filter attached. The samples were then acidified using a few drops of concentrated nitric acid (HNO_3) and stored until analyzed.

For Na adsorption studies, 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 ($NaHCO_3$) solution with a concentration of 1,010 mg/L as HCO_3^-. 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.

The water chemistry of the surrogate CBNG water (Table 4) was chosen by compiling published data from various sources (Rice *et al.* 2002, BLM 2003, King *et al.* 2004a) and prepared using appropriate amounts of inorganic chemicals and tetraethyl orthosilicate as the silicon (Si) source.

Table 4. Water Chemistry of the Synthetic CBNG Waters (mg/L)

Element	Na	Ca	Mg	K	Cl	SO_4	HCO_3	SiO_2	SAR	pH
CNBG Water I	205	10	2.5	1.25	45.4	5	505	5	15.5	8.20
CNBG Water II	411	10	2.5	2.5	65.8	10	1,010	10	30.1	8.90
CNBG Water III	822	10	2.5	2.5	65.8	10	1,010	10	60.2	8.90

CBNG water samples were also collected from different parts of PRB region and pooled to obtain a composite sample that had an SAR of 19. In order to evaluate exchange kinetics at high Na^+ levels typically encountered in northwestern PRB, Na^+ in the composite CBNG water was increased by adding Na_2CO_3. The two CBNG waters were evaluated for ion exchange kinetics with the zeolite materials. A factorial experiment with 4 zeolite materials and 2 CBNG water

qualities (SAR and EC) was conducted using the intermittent-flow columns using a mechanical vacuum extractor to keep the rate of leaching constant throughout experiment. Zeolite material was replicated 3 times and equal amount of zeolite material (50 g) was loaded into each of columns. Columns were leached with forty 50-ml volume increments of the respective CBNG waters. Leachate samples were analyzed for pH, EC, SAR, and the concentrations of soluble cations Na^+, Ca^{2+}, and Mg^{2+} with SAR calculated as:

$$SAR\ (mmol^{1/2}\ L^{-1/2}) = [Na^+]/\ [Ca^{2+} + Mg^{2+}]^{1/2} \tag{1}$$

where Na, Ca, and Mg represent millimolar concentrations of the respective ions ($mmol\ L^{-1}$).

The effect of sample particle size on Na^+ adsorption behavior was examined in adsorption studies using zeolites of varying particle sizes. Adsorption studies were conducted using the batch equilibration technique. A 5.0 g zeolites sample with varying particle size were weighed into 50 ml polyethylene bottles containing 45 ml of CBM water I, II, and III. The tubes were shaken on a reciprocal shaker for 48 hours, centrifuged, and the supernatant solution filtered and acidified.

Adsorption isotherms of Na-Wyoming zeolite for Ca^{2+} were also conducted using the batch equilibration technique (Zhao *et al.* 2004). A 5.0 g zeolite sample was weighed into 50 ml polyethylene bottles and spiked using stock $CaCl_2$ solution and the final volume is adjusted to 45 ml using DI water. The initial Ca^{2+} concentrations in the tubes ranged from 0 to 4,000 mg/L. The tubes were shaken on a reciprocal shaker for 48 hours, centrifuged, and the supernatant solution filtered and acidified as described above.

Packed Column Studies

Both intermittent and continuous flow-through column studies were utilized in order to predict zeolite performance under practical treatment system conditions. For the intermittent leaching studies, 50 ml columns containing zeolite were leached over a 24 hr period with 50 ml of CBNG water. This process was repeated 40 times. The continuous flow through column parameters were as follows: weight of zeolite: 132.0 g; column diameter: 25.0 mm; column length: 250 mm (for St. Cloud zeolite); 260 mm (for Bear River zeolite); flow rate: 3.0, 6.0, 16.0 ml/min; bed volume: ~125 cm^3. A smaller column with a column diameter of 15 mm, length of 400 mm was used for the WY-zeolite study at a flow rate of 5.0 ml/min. The effluents were collected using an automatic fraction collector.
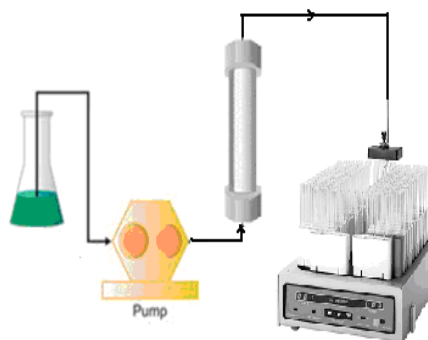
For WY-zeolite, which is naturally rich in Na^+, a pretreatment was carried out using 2 L of 0.1 M $CaCl_2$ solution that was passed through the columns at a flow rate of 3.0 ml/min, followed by rinsing using DI water. Column studies were carried out as described above.

Instrumentals

The concentrations of cations (Na^+, Ca^{2+}, Mg^{2+}) in solution were analyzed using Inductively Coupled Plasma (ICP) spectrophotometry (Thermo Jarrell Ash, model P300) and K^+ was analyzed using atomic absorption spectroscopy (Perkin Elmer, model 2380). The solutions were also measured for pH and electrical conductivity (EC).

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RESULTS AND DISCUSSION

STUDY 1 - Evaluation of Cation Exchange Reactions between CBNG Produced Water and St. Cloud Zeolites.

St. Cloud zeolites were available in 4 commercial sizes (4x6, 6x8, 6x14, and 14x40 mesh) that were readily available and had no additional costs associated with their use. Figure 3 shows the four different size zeolite materials used for column studies with the set up for the intermittent flow column experiments illustrated in Figure 4.
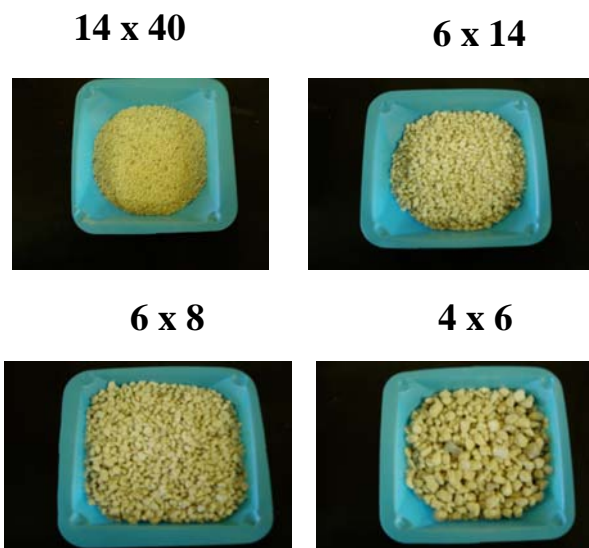
14 x 40   **6 x 14**

6 x 8   **4 x 6**

Figure 3. Different St. Cloud zeolite fractions used for column studies to evaluate cation exchange kinetics with CBNG water base cations.

Figure 4. Column experiment setup used to evaluate the cation exchange kinetics between CBNG water and different sizes of St. Cloud zeolites.

Content of the St. Cloud zeolite exchangeable cations are listed in Table 5. The effective CEC of St. Cloud zeolite materials ranged from 87 to 111 $cmol_c$ kg^{-1}. Although this CEC value is less than those obtained for other deposits surveyed in this study, St. Cloud zeolite deposits were naturally enriched with Ca^{2+}, which is the key to reduce SARs in CBNG water.

Table 5. Exchangeable cations concentrations ($cmol$ kg^{-1}) in St. Cloud Zeolite materials.

Exchangeable cation concentrations	4x6	6x8	6x14	14x40
Sodium (Na^+)	3	4	3	4
Potassium (K^+)	7	11	10	12
Calcium (Ca^{2+})	61	68	73	77
Magnesium (Mg^{2+})	17	15	17	18
Effective CEC ($cmol_c$ kg^{-1})	87	97	104	111

Cation exchange reactions between Zeolites and CBNG waters

St. Cloud zeolite materials performed extremely well in removing Na^+ from CBNG water samples both at low and high SAR conditions. After 50 ml of high Na^+ CBNG water was passed through the zeolites, Na^+ was reduced from 1129 to 53.4 (14x40 mesh) - 275 mg L^{-1} (4x6), Ca^{2+} from 43 (14x40) - 185 mg L^{-1} (4x6), and Mg^{2+} from 8.5 (14x40) - 19.8 mg L^{-1} (4x6). Leachates had SAR values that decreased from an initial value of 107 to 1.1 (14x40) - 9.7 (4x6) in case of high SAR CBNG water, and from 18.7 to 0.6 (14x40) - 3.4 (4x6) in case of low SAR CBNG water.

Figure 5 provides information on the cation exchange kinetics with progressive additions of high and low SAR CBNG water leached through zeolite samples. The Ca-rich zeolite materials removed significant amounts of Na^+ from CBNG waters both at low and high SAR conditions. Initial leaching of high Na^+ CBNG water through the zeolites resulted in a Na^+ reduction from 1129 to 53.4 mg L^{-1}. Leachate SARs decreased from an initial value of 107 to <1.0 in the case of high SAR CBNG water, and from 18.7 to 0.6 in the case of low SAR CBNG waters. Based on column exchange reactions using high Na^+ conditions, 1 tonne of zeolite material will reduce 750 barrels of CBNG water with an SAR of 34 (typically encountered in many parts of PRB region) to an accepted level of 10. Thus the zeolite technology is an efficient, effective and affordable water treatment alternative that maximizes the beneficial use of CBNG water.
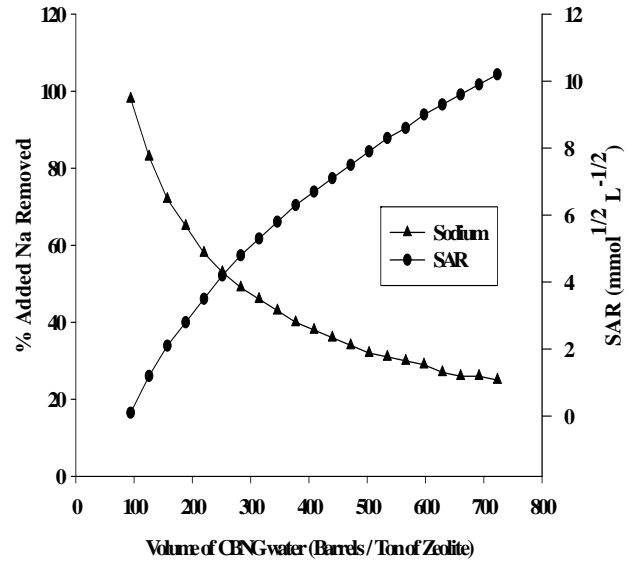

Figure 5. Reduction in cumulative CBNG water Na vs change in SAR using zeolite ion-exchange columns.

Based on the exchange kinetics obtained under high and low Na^+ conditions, 1 tonne of different particle size zeolite materials will reduce SAR of CBNG water from 34 (typically encountered in many parts of the PRB region) to accepted level of 10 is shown in Table 6.

Table 6. Volumes of CBNG water that can be treated by using 1 tonne of Zeolite to reduce SAR from 34 to a target value of 10.

Zeolite material	Liters	Gallons	Barrels
4x6	50,000	13,228	314
6x8	69,000	18,254	434
6x14	70,000	18,519	440
14x40	85,000	22,487	535

In summary, results obtained by the intermittent flow column studies indicated zeolite technology has the potential to reduce SARs to safe levels and may be used as a water treatment alternative that maximizes the beneficial use of CBNG produced water.

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STUDY 2 - Evaluation of Exchange Reactions Between Synthetic CBNG Water and Different Ca^{2+}-Rich Natural Zeolites.

Adsorption Kinetics

Sodium adsorption rates were faster for Bear River (BR) zeolite when compared to St. Cloud (ST) zeolite (Fig. 6). In addition, BR-zeolite removed more Na$^+$ and released greater amounts of Ca^{2+} than that of ST-zeolite. Other major exchangeable cations (i.e., K$^+$ and/or Mg^{2+}) can also be replaced by Na$^+$ in short term experiments. The adsorption kinetics are related to many factors including particle size, pore structure, and solute diffusion.
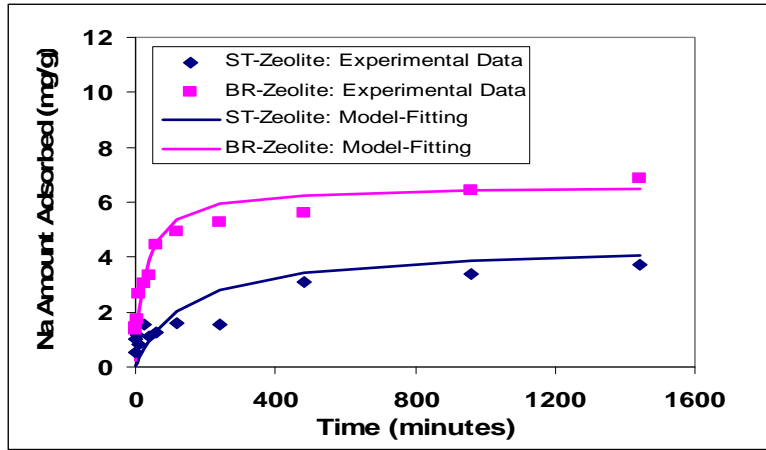

Figure 6. Na$^+$ adsorption kinetics and model fitting for ST-zeolite (14x40 mesh) and BR-zeolite (14x40 mesh)

Kinetics Modeling

Because adsorption kinetics is controlled by many factors, there have been many modeling approaches reported in the literature. Generally, two kinetic models of adsorption have been most frequently used: (1) active available site model and (2) chemical reaction rate model, which is based upon mass law concept. For many adsorption processes occurring on heterogeneous materials, it has been found that the pseudo-second-order kinetic equation agrees well with chemisorption as the rate-controlling step (Reddad *et al.* 2002, Ho and Mckay 1999, 2000). The pseudo-second-order kinetic rate equation can be expressed as (Ho and McKay 1999, 2000, Reddad *et al.* 2002):

$$\frac{dQ_t}{dt} = k*(Q_{eq} - Q_t)^2 \tag{2}$$

where Q_{eq} is the sorption capacity at equilibrium, Q_t is the solid-phase loading of Na$^+$ at time *t*, and *t* is time (min) and k (g/mmol*min) is the pseudo-second-order rate constant for the kinetic model. Considering the boundary conditions of $Q_t = 0$ (at $t = 0$) and $Q_t = Q_t$ (at $t = t$), the following linear equation can be obtained:

$$\frac{t}{Q_t} = \frac{1}{v_o} + \frac{1}{Q_{eq}}t \tag{3}$$

and

$$v_o = k*Q_{eq}^2 \tag{4}$$

where v_o (mmol/g∗min) is the initial adsorption rate. Therefore, by plotting t versus t/Q_t, the v_o and Q_{eq} values of kinetic study can be determined. A 24 hour equilibration period (1440 minutes) was found to be more than sufficient to establish steady state or equilibrium in sorption experiments using similar particle sizes and initial Na^+ concentrations. Results also suggested that equilibrium is obtained if the empty bed contact times (EBCT) are on the order of greater than 5 minutes.

Results were fitted using the pseudo-second-order kinetic model (Eq. 3) to estimate the rate constants, initial sorption rates, and adsorption capacities for Na^+. Relevant parameters are summarized in Table 7. The high fitting coefficients ($R^2 \sim 0.97$-0.99) indicated that the adsorption of Na^+ on the tested media could be well described using the pseudo-second-order kinetic model. Approximately 22% to 32% of the initial Na^+ in solution (about 411 ppm) was removed by the end of the 24-hr equilibration period. Rate constants and initial adsorption rates were higher for BR-Zeolite compared to ST-Zeolite. BR-Zeolite showed the highest equilibrium sorption capacity in the kinetic tests.

Differences among the zeolites are potentially attributable to differences in the physical and chemical properties of the media (i.e., composition, pore size, surface area, surface charge, sodium affinity, etc.). These adsorption kinetic parameters would be informative in predicting zeolite Na^+ removal from CBNG waters.

Table 7. Kinetic parameters for CBNG water Na^+ adsorption by zeolites using a pseudo-second-order kinetic model.

Media	R^2	k	v_o	Q_{eq} (mmol/g)	Q_{eq} (mg/g)
ST-Zeolite (14x40)	0.972	0.036	1.36×10^{-3}	0.195	4.47
BR-Zeolite (14x40)	0.999	0.127	1.05×10^{-2}	0.287	6.60

R^2= Model-fitting coefficient;
K = The pseudo-second-order rate constant for the kinetic model (g/mmol∗min);
v_o = Initial adsorption rate (mmol/g∗min);
Q_{eq} = The sorption capacity at equilibrium ($mmol_{As}$/g) or mg/g.

Data Analysis for Diffusion Coefficients

Diffusion coefficients are also an important parameter in predicting the diffusion rate of adsorbate molecules in porous media (Siegel *et al.* 2007). In order to extract the effective diffusivity of Na^+ in the macropores of adsorbent media, a diffusion equation for a macropore-controlled system on a spherical shell element of the adsorbent particle was proposed Ruthven (1984):

$$(1-\varepsilon_p)\frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial c}{\partial t} = \varepsilon_p D_p \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R} \right) \tag{5}$$

where ε_p is adsorbent particle porosity, q(R, t) is the adsorbed phase concentration (µg/L of adsorbate), t (s) is time, c (µg/L) is the adsorbate concentration in the supernate, D_p (cm^2/s) is the macropore diffusivity of adsorbate in the adsorbent, and R (cm) is the radial distance from the center of the adsorbent particle. The macropore diffusivity (D_p) is assume to be independent of

concentration in the above equation. For fractional adsorption uptake M_t/M_{max} above 70%, the solution for the equation with a 2% error is given by (Siegel *et al.* 2007):

$$\frac{M_t}{M_{max}} \cong 1 - \frac{6}{\pi^2} \exp\left(\frac{\pi^2 D_e t}{R_p^2}\right) \tag{6}$$

where M_t (µg/L) is the mass gain of adsorbate at time t, M_{max} (µg/L) is the mass gain of adsorbate at infinite time, and D_e (cm^2/s) is the effective diffusivity defined by:

$$D_e = \frac{\varepsilon_p D_p}{\varepsilon_p + (1 - \varepsilon_p)K} \tag{7}$$

A plot of Ln(1-(M_t/M_{max})) vs. time should generate a straight line with a slope of $\left(\frac{-\pi^2 D_e}{R_p^2}\right)$ and

an intercept of $Ln\left(\frac{6}{\pi^2}\right)$, from which the effective diffusivity, D_e, for Na$^+$ diffusion in the macropores of the media can be calculated.

The values for effective diffusivity D_e (cm^2/s) calculated based on data points with M_t/M_{max} above 40% assuming an average particle size of 0.315 mm, are 2.01×10^{-9} ($R^2=0.939$) for ST-zeolite (14x40) and 7.03×10^{-9} ($R^2=0.948$) for BR-zeolite (14x40), respectively. BR-zeolite has a higher D_e value than that of ST-zeolite (Table 8).

Table 8. Effective Na$^+$ diffusivity for ST-Zeolite and BR-Zeolite samples of varying particle sizes.

Particle Size (mesh)	D_e (cm^2/s)	R^2
ST-Zeolite (14x40)	2.01×10^{-9}	0.939
BR-Zeolite (14x40)	7.03×10^{-9}	0.948

Adsorption Isotherms

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

$$q = \frac{q_{max} KC}{1 + KC} \tag{8}$$

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. Rearranging to a linear form, Equation 1 becomes:

$$\frac{C}{q} = \frac{1}{Kq_{max}} + \frac{C}{q_{max}} \tag{9}$$

Plotting $\frac{C}{q}$ *vs* C, the slope is $\frac{1}{q_{max}}$ and the intercept is $\frac{1}{Kq_{max}}$.

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 for ST-zeolite and BR-zeolite were 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 (Table 9). 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 9. Langmuir adsorption parameters for the adsorption of Na^+ by ST-Zeolite (14x40) and BR-Zeolite (14x40)

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

Zeolite cation adsorption behavior (i.e., adsorption capacity and selectivity) is 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 stronger adsorption sites. The higher K^+ in BR-zeolite suggest that it could occupy the stronger adsorption sites thus leaving the Ca^{2+} in relatively weak adsorption 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 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 as was shown for ST-zeolite in study 1.

Packed Column Study and Data Analysis

Results of the column studies at flow rate of 3.0 ml/min (Figure 7) were consistent with the tendency observed in the batch adsorption kinetic/isotherm studies (Study 2). Monitoring of the effluent solution pH indicated that, as compared to that of the influent solution (pH=8.90±0.10), there was no significant change in pH values of the leachates for ST-zeolite (pH=9.00±0.30) and for BR-zeolite (pH=8.90±0.10). The BR-zeolite removed greater amounts of Na^+ from the synthetic CBNG waters and 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.
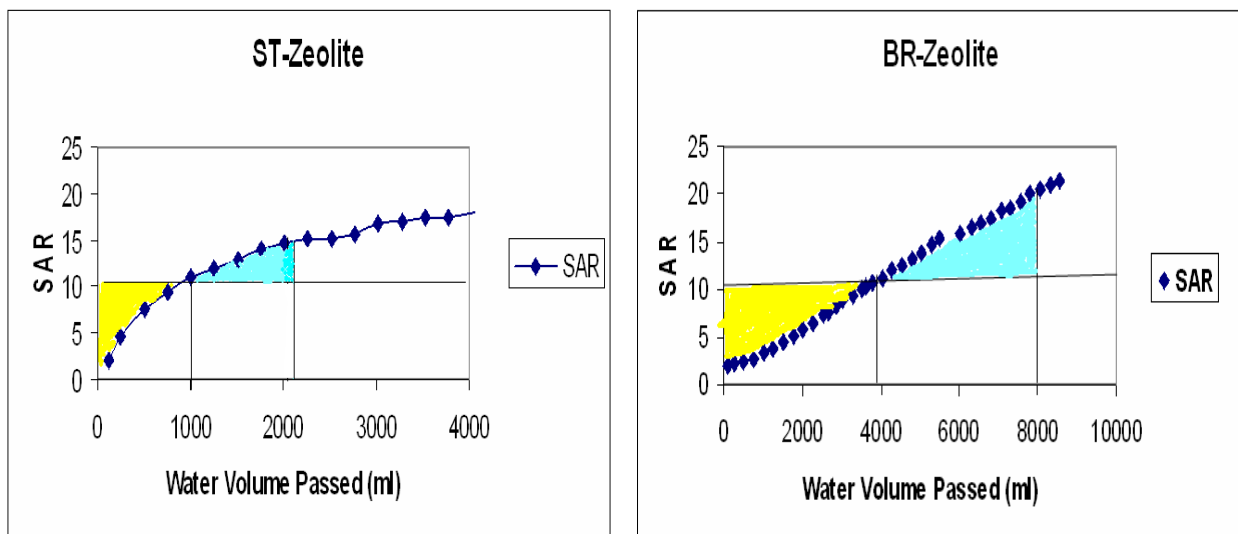
Figure 7. Estimation of cumulative treatable water volume by ST-zeolite and BR-zeolite

Another interesting finding relates to our studies on an Arizona (AZ) chabazite. Though Ca^{2+} is the dominant exchangeable cation, almost no Na^+ was removed in the column study, suggesting that the Ca^{2+} in the chabazite is strongly adsorbed. This may be attributed to the upgrading treatment of the raw materials with is naturally Na-rich chabazite.

If one considers CBNG water with SAR values equal to or less than 10 to be suitable for land application, using SAR breakthrough curves can estimate the efficiency of flow-through zeolite treatment systems for this purpose. The amount of the synthetic CBNG water (SAR=30 $mmol^{\frac{1}{2}}$ $L^{-\frac{1}{2}}$) that can be treated per tonne (1,000 kg) of ST-zeolite and BR-zeolite would be about 8,000 and 30,000 L, respectively. On the other hand, if CBNG water with an effluent SAR of 10 $mmol^{\frac{1}{2}} L^{-\frac{1}{2}}$ 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 SAR=10 cutoff line (yellow area in Figure 7), the amount of additional CNBG waters that could be treated and combined with the initially processed waters to reach a final SAR value of 10 can be estimated. Extrapolating the results suggests that one tonne (1,000 kg) of ST-zeolite and BR-zeolite can treat approximately 16,000 and 60,000 L of the synthetic CBNG water (SAR=30), respectively, to a final SAR around 10, which is considered safe for land application for agricultural use.

Regeneration Using 0.1 M CaCl₂ Solution

A majority (~90%) of adsorbed Na^+ by BR-zeolite can be replaced by Ca^{2+} after passing 1 L 0.1M $CaCl_2$ solution (Ca^{2+} = 4000 ppm) (Fig. 8). It is anticipated that increasing the regeneration $CaCl_2$ solution concentration could result in less $CaCl_2$ solution used as well as less spent brine generated.

Results from 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. These factors must be considered in studies evaluating the ability of zeolites to reduce Na^+ in CBNG waters.
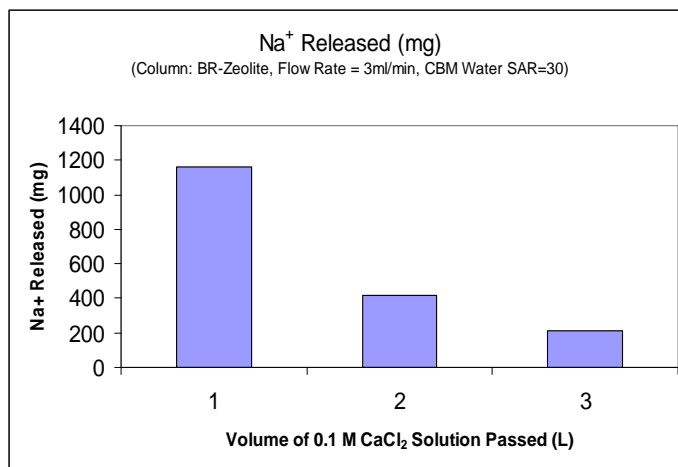
Figure 7. Regeneration of Spent BR-Zeolite Column by 0.1 M CaCl₂ Solution

STUDY 3-Natural Na-rich Zeolite (Wyoming)

Ca²⁺ Adsorption Isotherms by WY-zeolite

The Ca²⁺ adsorption isotherm curves displayed L-type adsorption on WY-Zeolite. The L-type isotherms are described well using the Langmuir equation (Eq. 3). The maximum amount of adsorption by WY-Zeolite is 10.3 mg/g, accounting for ~25% of the measured CEC value (Table 10).

Table 10. Langmuir adsorption parameters for the adsorption of Ca²⁺ by natural WY-zeolite

Sample	q_{max} (mg/g)	K	R^2
WY-Zeolite	10.3	2.2	0.999

In a previous study, Hulbert (1987) investigated Na⁺, Ca²⁺, and NH₄⁺ exchange on the same zeolite materials collected from an outcrop of blue-green tuff in the Fort LaClede deposit, Sweetwater County, WY. Hulbert (1987) found that Ca²⁺ replaces Na⁺ with decreasing selectivity as Ca²⁺ loading increases to about 80% at 30ºC (95% at 63ºC, above which the selectivity reverses). The standard free energy of replacement of two Na⁺ ions by one Ca²⁺ ion in 0.05 M solutions was 1.2 ± 0.2 kcal/mole at 63ºC and -0.3 to -0.8 kcal/mole at 30ºC. These results suggest the Fort LaClede clinoptilolite has a moderate selectivity for Ca²⁺ over Na⁺ at <80% Ca²⁺ loading and 30ºC. Above this loading, the zeolite is slightly selective for Na⁺. At 63ºC the zeolite has somewhat greater affinity for Ca²⁺ at all loadings than it does at 30ºC. These properties are important when considering a system for treating CBNG waters.

Figure 9 also demonstrates that a majority (~90%) of the originally adsorbed Na⁺ in WY-zeolite could be replaced by Ca²⁺ after passing ~2 L 0.1M CaCl₂ solution (Ca²⁺=4,000 ppm).
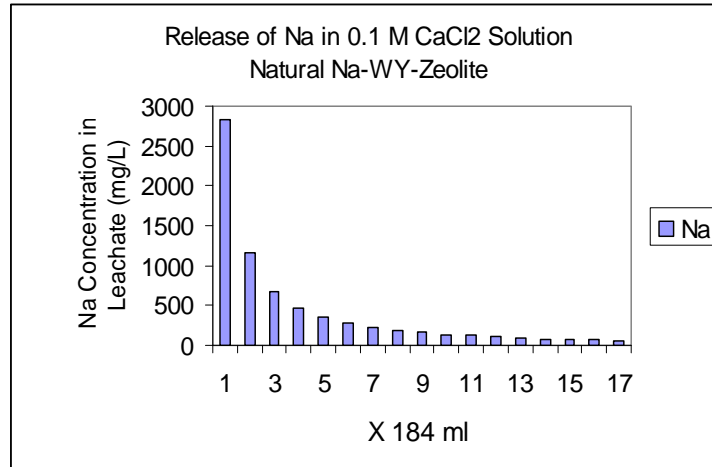
Figure 9. Pretreatment of Na-WY-Zeolite Using 0.1 M CaCl$_2$ solution in a packed column: Release of Na (x-axis: The solution volume of each collection is 184 ml)

Packed Column Studies using Ca^{2+}-Pretreated WY-zeolite

Upon pretreatment with CaCl$_2$, the Na$^+$ WY-zeolite was converted to a Ca-rich zeolite. It was estimated that one metric tonne (1000 kg) of the pretreated WY-zeolite can treat ~120000 L (~32000 gallons or ~750 barrels) CBM water to reduce its SAR from 30 to acceptable 10 (Fig 10). It is interesting to note that the treatment capacity of pretreated WY-Zeolite is ~1.6 times higher than the BR-Zeolite, which is consistent with CEC measurements.
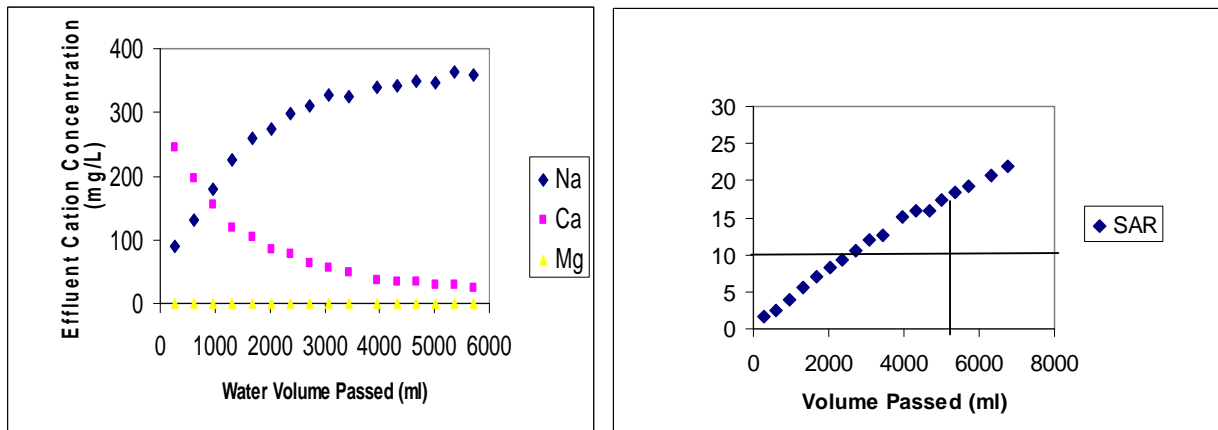

Figure 10. Column breakthrough curves for pre-modified (Ca^{2+}-treated) WY-Zeolite and corresponding water SAR upon treatment.

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TECHNOLOGY FEASIBILITY ANALYSIS

The following evaluation of current CBNG water treatment technologies (Table 11) and associated operation costs (Table 12) are adapted from Chris Johnston (2006).

Table 11. Costs associated with CBNG co-produced water management, US DOE, 2002).

Management Technology	Capital Costs	O & M Costs
Surface Discharge	$300	$0.004/bbl
Infiltration/Storage Ponds	$10,300/well (DOE)	$0.06/bbl (DOE)
Shallow Injection	$6,350	$0.045/bbl
Deep Injection	$62,500	$0.095/bbl
Reverse Osmosis	$77.14/bbl	$0.033/bbl

Table 12. Capital and O&M costs associated with managed irrigation.

Item	Capital Costs	O&M Costs
Irrigation Systems (16.2 ha)		
Center Pivot System	$58,000	$0.04/bbl
Side Roll Systems	$55,000	$0.12 - $1.20/bbl
Automated Big Gun System	$55,000	$0.04 - $0.08/bbl
Manual Big Gun System	$20,000	$0.20 - $0.40/bbl
Water Treatments		
Gypsum Applicator		
175 gallon	$2,959	$0.02/bbl
325 gallon	$2,870	$0.02/bbl
525 gallon	$3,200	$0.02/bbl
Pump and Metering Box	$2,000	
Sulfur Burner	$30,000	$0.08/bbl
Mixing Tank	$1,500	
Pumps (2)	$200-$300 each	
Soil Amendments		
Gypsum and Sulfur (delivered) (1.45 Mg/ha)		$0.12 -$0.15/bbl

The uses for natural zeolites can be generally categorized into different functional classifications, and within each exists a broad range of applications (Figure 11).

Prices for natural zeolite vary with zeolite content and processing. Unit values for 2005 zeolite market, obtained through the U.S. Geological Survey canvass of domestic zeolite producers, ranged from $50 to $140 per metric tonne. The bulk of the tonnage sold ranged from $80 and $140 per tonne. Eyde and Holmes (2006, p. 1058) reported that prices for industrial or agricultural applications ranged from $30 to $70 per tonne for granular products down to 40 mesh and from $50 to $120 per tonne for finer (-40 to +325 mesh) ground material. Quoted prices should be used only as a guideline because actual prices depend on the terms of the contract between seller and buyer.

As might be expected, the production cost for natural clinoptilolite zeolite material varies with the size desired, amount to be purchased, and mode of transport. The average cost to produce a size fraction of 14x40 (material which will pass through a 14 mesh sieve but not through a 40 mesh sieve) is approximately $100.00 per tonne, prior to transporting. Depending on actual miles traveled, transport costs would likely run between $50.00 and $100.00 per tonne, delivered to the PRB.

Based on our results, the cost of treating CBNG water with ST-zeolite is around $0.80-1.00 per barrel, and for BR-zeolite approximately $0.20-0.40 per barrel, not including other expenses. BR-zeolite also provides K^+ which is an important plant nutrient. The locally available zeolite WY-Zeolite is naturally Na-rich, therefore, pretreatment of the samples by converting it to Ca-rich is necessary. The cost for the WY-zeolite should be around $0.10-0.20 per barrel, not including the pretreatment expenses. However, if regeneration and reuse of the media are to be considered, the treatment cost should even be lower.

It is well know that zeolite has many applications as adsorbents in agriculture, water treatment, aquaculture, household products, industry and air/gas treatment (Figure 11). For example, zeolite is used for products such as pet litter, fish tank media, or odor control applications, with prices ranging from $0.50 to $4.50 per kilogram. Therefore, by exploring applications of the spent zeolite media for other uses, both locally or nationwide, there could be a significant reduction in the treatment cost, making the use of zeolite treatment a more feasible, cost-effective technology in CBNG water treatment.
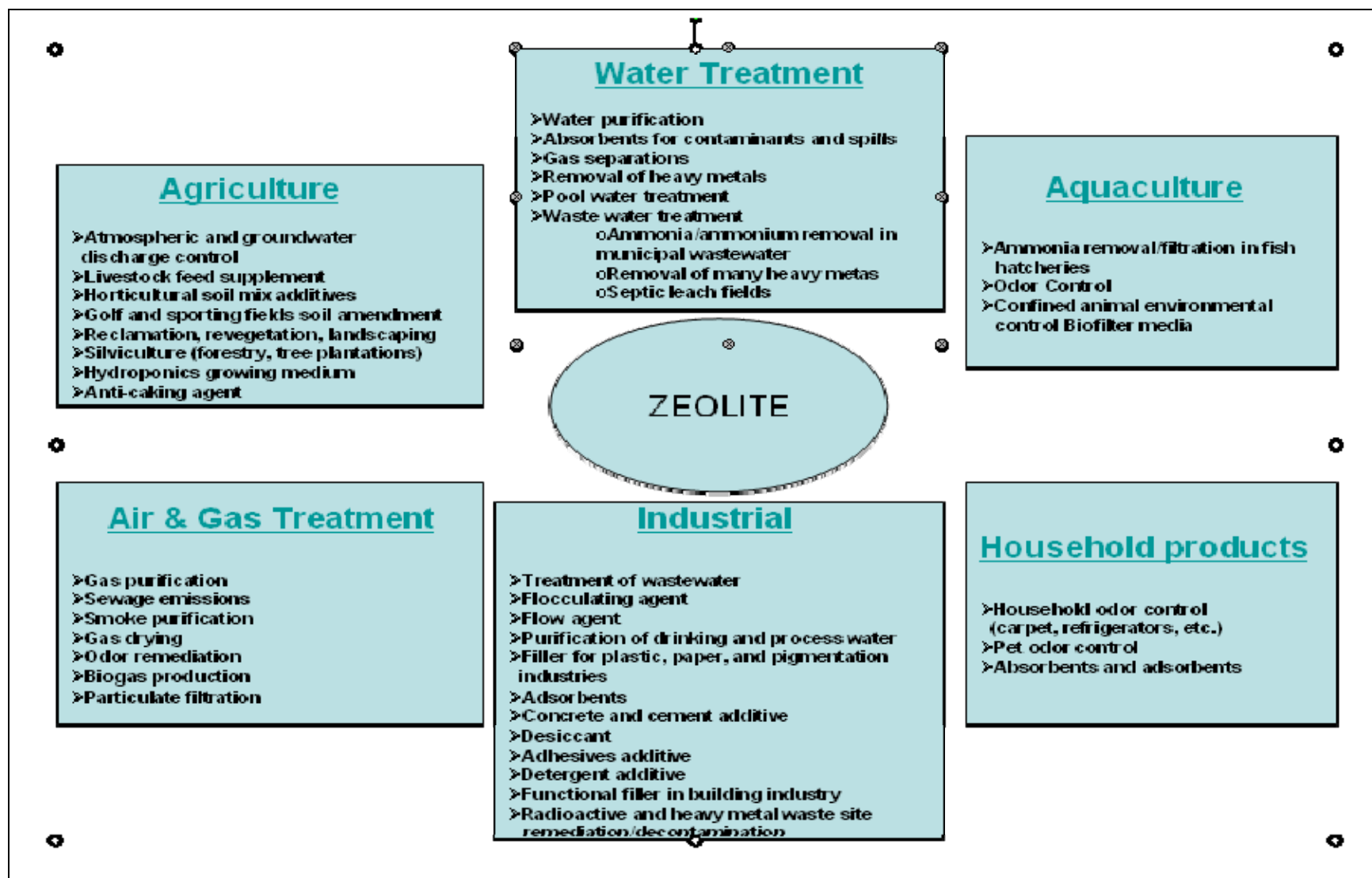
Figure 11. The various applications of zeolite products.

CONCLUSIONS

In this study, the potential utilization of Ca^{2+}-rich natural zeolites and modified Na^+-rich natural zeolites were examined for removal of Na^+ from CBNG waters. Zeolite samples examined were from New Mexico, Idaho, Arizona and Wyoming. The zeolite materials were used as received or pre-modified in adsorption kinetic/isotherm studies and column experiments. Both CBNG waters and surrogate waters that simulated the chemistry of CBNG waters were 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, $mmol^{\frac{1}{2}} L^{-\frac{1}{2}}$) of the simulated CNNG water from 30 to an acceptable level of 10. 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. However, an upgraded Ca^{2+}-rich chabazite from Arizona shows no removal of Na^+ from CBNG waters.

Studies also included a natural Na-rich zeolite from Wyoming. The WY-zeolite was pretreated using $CaCl_2$ solution and converted to a Ca-exchanged zeolite before use. The Ca^{2+} batch adsorption isotherm curves showed L-type adsorption. The maximum amount of Na^+ adsorption by WY-Zeolite was 10.3 mg/g, accounting for ~25% of the measured CEC value. Column studies indicated that one metric tonne of the Ca-Wyoming zeolite can treat ~1.2×10^5 L (~3.2×10^4 gallons) CBNG water to reduce its sodium adsorption ratio (SAR, $mmol^{\frac{1}{2}} L^{-\frac{1}{2}}$) from 30 to an acceptable level of 10. Compared to results of the other zeolites (ST-Zeolite ~1.6×10^4 and BR-Zeolite ~6.0×10^4 L, respectively), it is suggested that water treatment with locally available Wyoming zeolite appears to be more effective and may be a promising and feasible treatment technology for maximizing the beneficial use of poor-quality CBNG in the Powder River Basin, WY. An innovative integrated system using Na-Wyoming zeolite is currently being developed.

The major accomplishments of this CBNG water treatment study include an invention disclosure, and several conference presentations and journal manuscripts (see section below). Ongoing studies are evaluating water treatment techniques involving the direct application of zeolite to CBNG waters and development of a field scale prototype.

Accomplishments

- Collected several zeolite minerals from Wyoming and the other states including California, Idaho, Nevada and New Mexico;
- Assessed feasibility of zeolite deposits in terms of mineral quality and quantity;
- Conducted numerous field studies to follow-up on research on zeolite occurrences reported in the literature;
- Eliminated several reported occurrences as potential sources for zeolite for the purposes proposed for this project;
- Characterized ten natural zeolite materials using X-Ray diffraction for mineralogical compositions and wet chemistry methods for total elemental composition, CEC and exchangeable cations;

- Extensively studied the three most promising zeolite samples to evaluate their potentials for CBNG water treatment. They were two naturally Ca^{2+} rich zeolites from New Mexico and Idaho, and one naturally Na^+-rich zeolite from Wyoming that was subjected to pre-modification before use;
- Conducted both adsorption kinetic and isotherms studies with the data analyzed and fitted to models in order to evaluate the potential of the different zeolites for treating CBNG waters;
- Performed a series of packed column studies to determine the effect of particle size, water chemistry, and flow rate on Na^+ removal from CBNG water;
- Evaluated the possibility of direct application of zeolite to CBNG water reservoirs or ponds using a large fish tank;
- Determined that the volume of CBNG water that could be treated by the zeolites decreased in the order of: Ca-Modified-Wyoming zeolite > Idaho Bear River Ca-zeolite > New Mexico St. Cloud Ca-zeolite;
- Attributed the variation in zeolite performance for CBNG water treatment to mineralogical composition, CEC, Na^+ effective diffusivity, particle size, etc. of the zeolite samples;
- Performed an analysis on the economic feasibility of using zeolite treatment as a potential feasible, cost-effective technology in CBNG water treatment;
- Disseminated information on our findings, progress of the project as well as information on the physical and chemical nature of zeolites to conference attendees, students, general public (via inquiries, website visits, etc.);
- Began compilation of WSGS publications on zeolites and their occurrences and applications (to be published by fall, 2007);
- Continuing studies that include the design and testing of a field scale prototype.

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Student/Staff Support

The following individuals were involved in this project.

Kaitlin Forbotnik – Laboratory Assistant
Shannon Geslin – Laboratory Assistant
Girisha Ganjegunte - Post Doctoral Research Scientist
Robert Gregory – Geology Graduate Student
Ray Harris – Geologists (deceased)
David Micale – Research Associate
Steve Wilkins – Soil Science Graduate Student
Michael Urynowicz – Assistant Professor
Hongting Zhao – Post Doctoral Research Scientist

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Additional funding was received for a two year project to develop a laboratory prototype and field-scale model for treating CBNG water using the zeolite treatment technology. The principal investigators of this project are Drs. George Vance and Michael Urynowicz, Assistant Professor of Civil and Environmental Engineering, with Dr. Ron Surdam as a collaborator. We expect to provide support for a doctoral candidate from the project grant.

George Vance received a sabbatical leave grant from the USDA National Research Initiative program to support zeolite research involving the treatment of various waters. His sabbatical was funded for January to August, 2007. He has spent some of his sabbatical at New Mexico Institute of Mining and Technology working with Dr. Robert Bowman, Department Head of Earth and Environmental Sciences. Dr. Bowman has extensive experience on the use of surfactant modified zeolites for environmental protection.
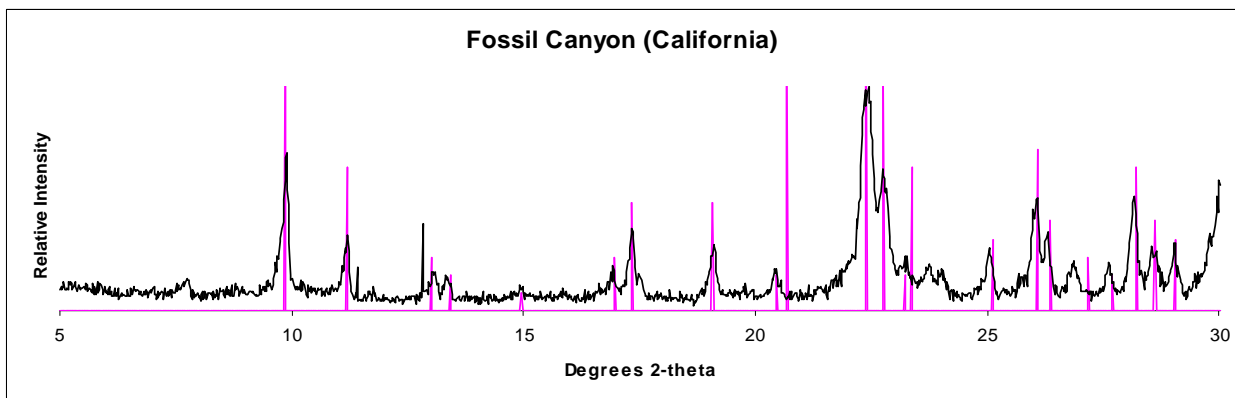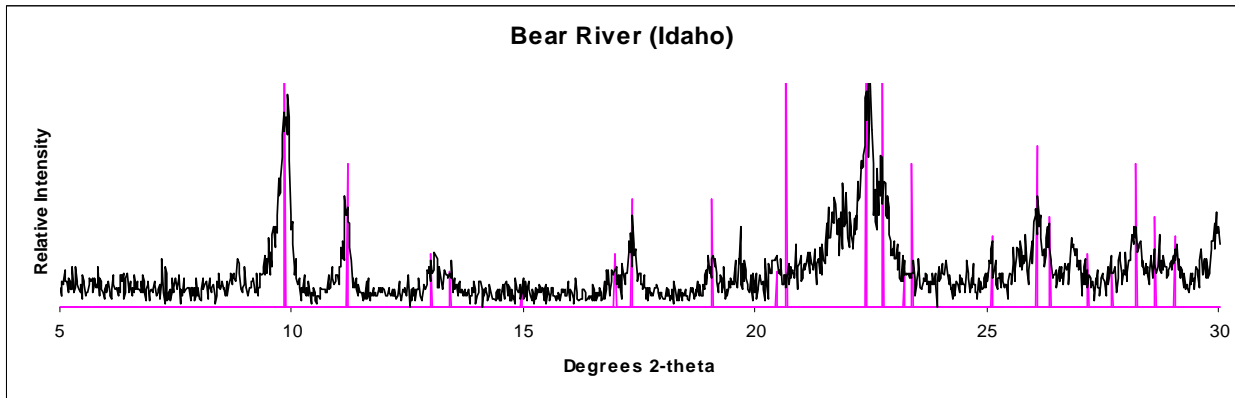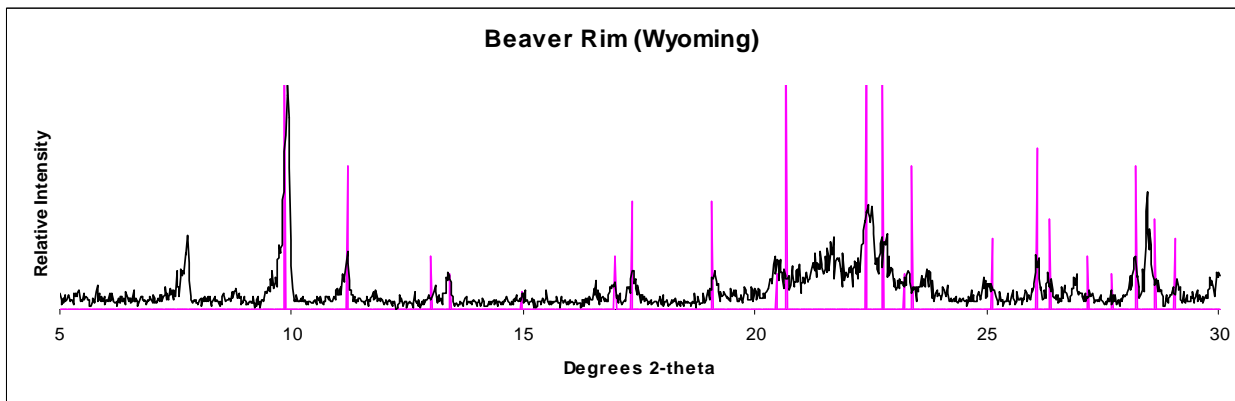
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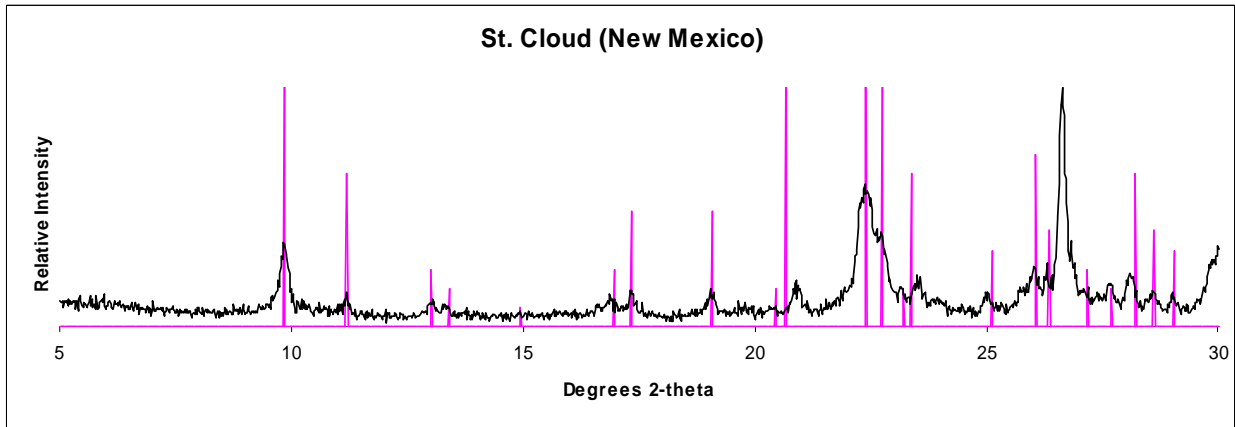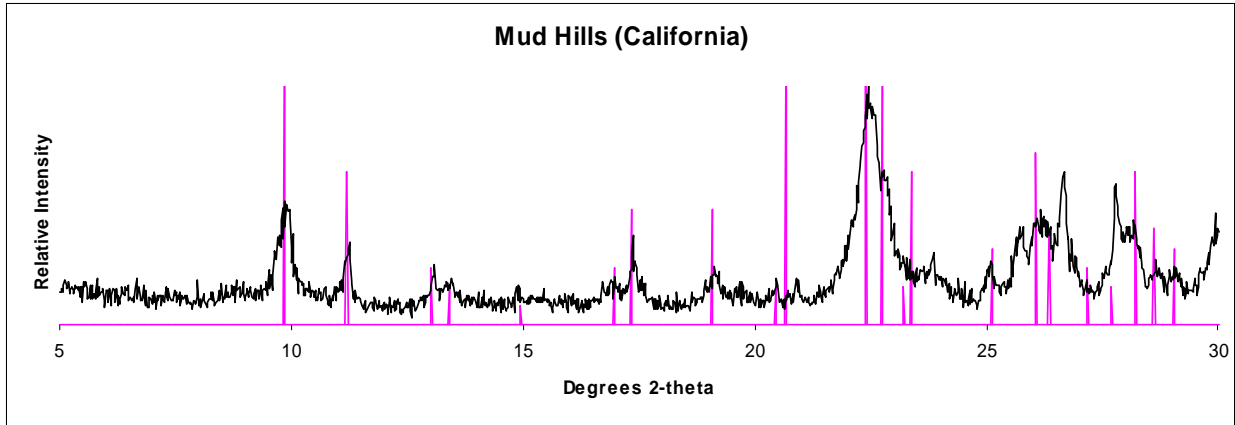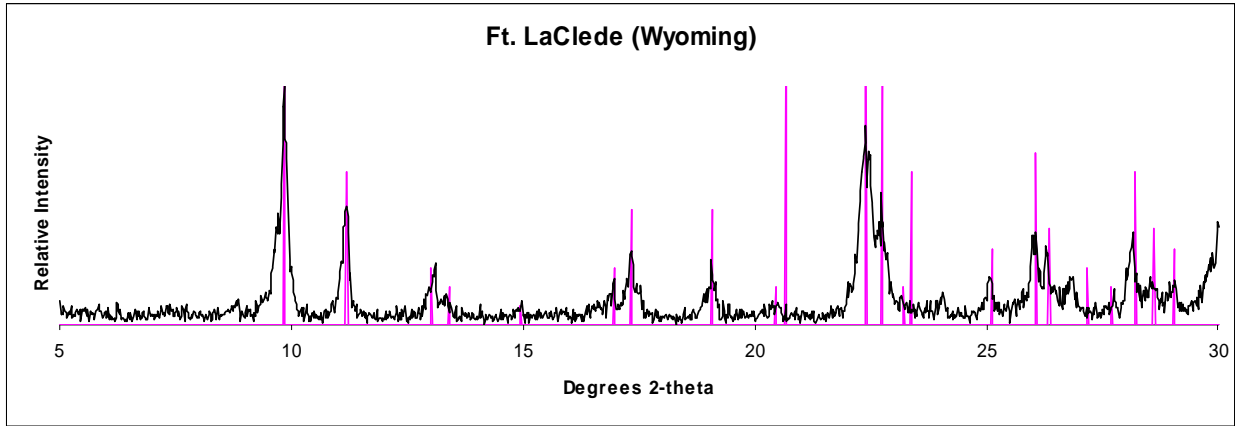*Proceedings and Abstracts with Presentations*

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Appendix I Zeolite Diffractograms.

Ash Meadows (California-Nevada)

Beaver Rim (Wyoming)

Bear River (Idaho)

Fossil Canyon (California)

Ft. LaClede (Wyoming)

Mud Hills (California)

St. Cloud (New Mexico)

APPENDIX II

Results of whole-rock analysis done by ALS-Chemex, Inc., Vancouver, B.C.

	AM1 - 1643	AM1 - 2035	AM1 - C	BC1-06	BRZ1	FC1	FC2a	FC2b	FL1-06	MH1	SC1
Whole Rock Analyses											
Weight %											
SiO_2	65.3	65.3	65.3	60.3	66.5	61.2	61.8	61.7	62.7	64.2	66.9
Al_2O_3	10.3	10.45	10.5	11.85	10.4	12.25	11.9	12.05	12.15	11	11.95
Fe_2O_3	0.82	1.06	0.82	2.44	1.99	1.34	0.79	0.88	0.5	0.88	1.44
CaO	0.86	0.75	0.97	1.68	2.33	1.72	0.94	0.9	1.5	1.41	2.87
MgO	0.4	0.39	0.4	4.78	0.57	1.28	0.69	0.88	0.3	0.52	1.2
Na_2O	3.41	3.48	3.47	1.6	0.49	3.11	4.27	4.19	4.4	3.57	0.44
K_2O	3.6	3.66	3.73	2.91	4.32	1.78	1.74	1.55	1.53	1.63	3.44
Cr_2O_3	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
TiO_2	0.09	0.09	0.09	0.28	0.28	0.21	0.1	0.1	0.17	0.13	0.21
MnO	0.04	0.04	0.03	0.03	0.03	0.01	0.01	0.04	<0.01	0.04	0.07
P_2O_5	0.02	0.01	0.03	0.07	0.01	0.04	0.02	0.02	0.03	0.04	0.06
SrO	0.03	0.03	0.05	0.02	0.02	0.16	0.56	0.59	0.04	0.27	0.17
BaO	0.03	0.03	0.03	0.07	0.12	0.27	0.35	0.34	0.13	0.22	0.08
LOI	12.65	12.5	12.55	13.75	12.5	14.65	14.4	14.6	15.05	13.75	11.1
Total	97.6	97.8	98.0	99.8	99.6	98.0	97.6	97.9	98.5	97.7	99.9

Results of minor and trace element analysis done by ALS-Chemex, Inc., Vancouver, B.C.

Sample		AM1 - C	AM1 - 2035	AM1 - 1643	FC1	FC2a	FC2b	MH1	SC1	BC1-06	BRZ1	FL1-06	PB1-06
Element	units												
Ag	ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
As	ppm	8	8.7	9.1	4.4	3.5	2.4	8.6	2.3	3.4	2	1	0.5
Ba	ppm	240	260	300	2280	3130	3050	1890	660	636	1020	1160	296
Bi	ppm	0.12	0.15	0.13	0.15	0.22	0.18	0.14	0.29	0.19	0.43	0.19	0.17
Ce	ppm	54	52.6	58.3	94.3	59	72	53.3	76.2	50.2	150.5	87.2	67.1
Co	ppm	0.6	0.8	0.6	2.3	0.5	0.5	0.7	2.6	2.6	1.1	1.1	3.1
Cr	ppm	42	67	22	10	<10	<10	<10	17	10	<10	<10	10
Cs	ppm	2.81	3.03	3.13	1.14	0.38	0.33	91.4	3.89	5.17	3.87	2.18	5.84
Cu	ppm	2.7	8.4	4.9	9.7	10.8	6.6	8.7	7.6	38	7	12	14
Ga	ppm	14.05	13.7	13.8	15.95	17.25	16.25	17.5	15.95	14.5	18.6	14.1	17.3
Hf	ppm	3.2	3.1	3.2	4.1	4.4	4.8	3.7	4.4	4.5	11.7	7	4.7
La	ppm	27.7	26.4	28.8	52.9	29.6	34.3	26.6	37.7	28	77.8	47.1	35.1
Mo	ppm	<2	<2	<2	<2	<2	<2	<2	<2	3	<2	<2	3
Nb	ppm	13.4	13.4	13.3	10	21.5	15	19.6	21.3	10.6	45.6	29	19.6
Ni	ppm	1.4	2.9	1.1	2.5	0.6	0.5	0.8	5.8	5	<5	<5	7
Pb	ppm	21	21.7	23.4	32.8	12.9	10.3	17.8	28	22	24	19	23
Rb	ppm	103	106.5	109	31.9	42.1	34.9	114.5	106.5	101	160	71.1	175.5
Sb	ppm	0.64	0.72	0.65	0.72	0.29	0.24	0.91	0.31	0.16	0.71	0.11	0.08
Se	ppm	1	1	2	2	1	2	1	2	<1	<1	<1	<1
Sn	ppm	1.8	1.8	1.8	2.5	2.4	2.9	2.5	2.5	2	7	3	3
Sr	ppm	387	276	285	1395	4950	5290	2280	1475	167	164	401	135
Ta	ppm	1.18	1.15	1.14	1.4	1.48	1.68	1.35	1.74	1.2	3.3	1.7	1.6
Te	ppm	<0.05	<0.05	<0.05	<0.05	0.06	0.05	<0.05	<0.05	<0.01	0.01	0.01	0.01
Th	ppm	18	17.2	18	19	18.1	23.5	13.6	22.7	19.45	27	18.1	23.7
Tl	ppm	0.52	0.55	0.6	0.23	0.05	0.04	0.3	0.57	<0.5	0.7	<0.5	0.8
U	ppm	2.6	2.5	2.6	2.2	0.2	0.2	1	2.6	5.27	6.49	5.01	6.73
V	ppm	6	7	6	15	46	43	8	13	27	<5	6	16
W	ppm	1.1	1.5	1.1	0.3	0.2	0.1	0.3	0.6	2	3	2	2
Y	ppm	11.5	12	13.8	16.4	9.1	11.6	12.3	26.6	15.1	54	22.7	21.1
Zn	ppm	24	24	23	66	56	61	52	44	34	43	40	45
Zr	ppm	79.7	78.1	77.6	83	109	110	78.7	106.5	143	398	231	131