



BEAR RIVER **ZEOLITE** BRZ™

OIL AND GAS FIELD APPLICATIONS

BEAR RIVER **ZEOLITE** BRZ™:

- Holds up to 30% of its weight in oil
- Holds 55% of its weight in water
- Is more effective than sand for traction due to the angular and lighter grains



RIG MAINTENANCE

LOCATION MAINTENANCE

DRYING AND SOLIDIFYING CUTTINGS

PRODUCED WATER AND FLOWBACK WATER

SURFACE MODIFIED BRZ™ (SMZ)

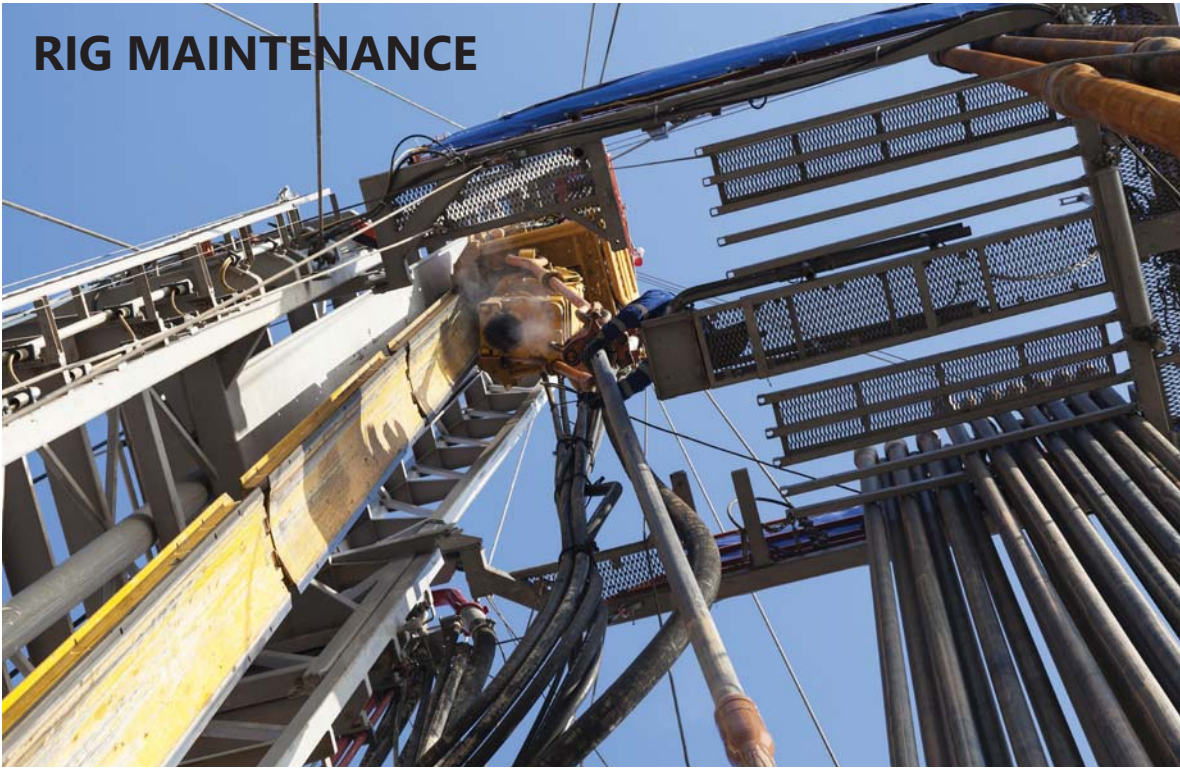
OIL SPILL AND BLOWOUT REMEDIATION

HYDROGEN SULFIDE CONTROL

PRESSURE SWING APPARATUS

HIGH SALINITY SOIL

RIG MAINTENANCE

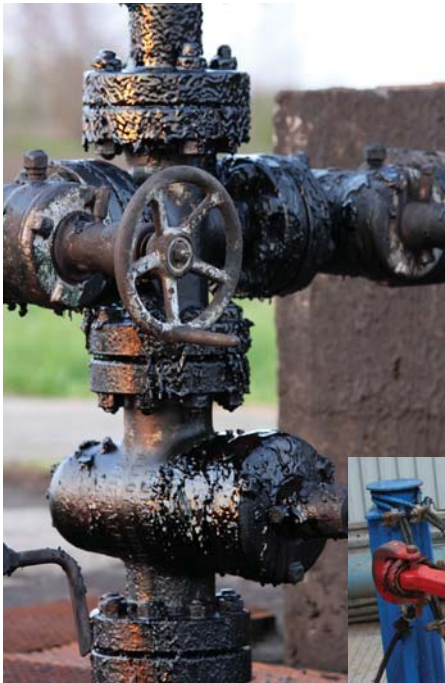


Derrick

APPLICATIONS

BRZ™ can be used to absorb oil, antifreeze, liquid chemicals, fuel, solvents, sewage, biohazard fluids (blood, etc.) on traffic areas, work surfaces, tools, and equipment. The fine particles left after clean-up provide traction for floors, stairs, etc. and grip control for equipment and tools.

Packaging	Shaker bottles, 25 or 50 pound bags, 1 ton totes, and bulk
Particle Sizes (mesh)	14 x 40, -40



Valves



Rig tong



Slips

Cleaning

Clean slips, tongs, motors, draw-works, drill collars, subs, drill pipe, and tools. Clean equipment and tools with BRZ™ to remove oil and fluids. Highly effective for invert drill mud clean-up.



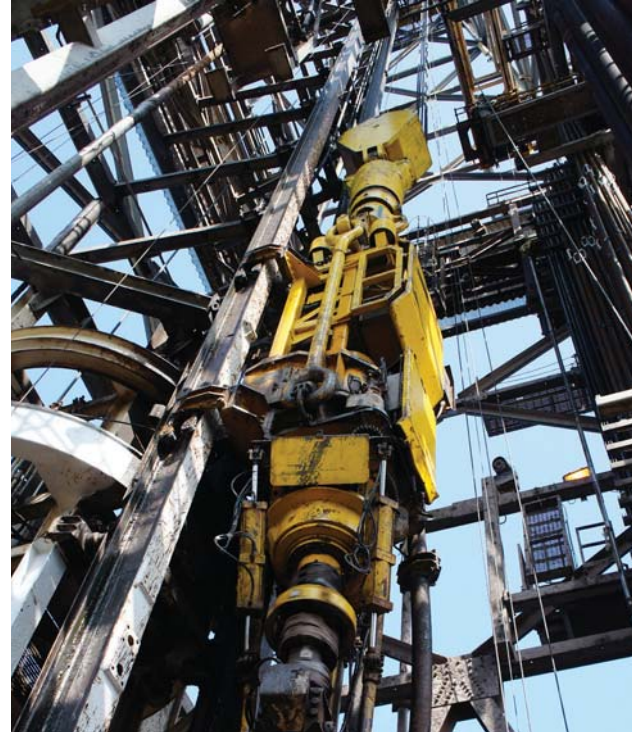
Blowout preventer

Spills and Blowouts

Oil, antifreeze, liquid chemicals, fuel, solvents, sewage, biohazard fluids: Completely cover the spill with BRZ™ allowing time for fluid absorption. Concrete walkways and steel floors may need more than one application.



Drill pipe



Top drive

Traction

For steel floors and walkways covered with invert mud, drill mud or ice. Also increases grip for tool handling, railings, and pipe.

LOCATION MAINTENANCE



Drilling location

APPLICATIONS

- Clean up all liquid spills
- Dry wet areas, such as peripheral trenches
- Traction control on ice and snow
- Deodorize porta-potties, sewage, and garbage

DRYING AND SOLIDIFYING CUTTINGS

APPLICATIONS

Drill cuttings can be dried and solidified by mixing in BRZ™. BRZ™ treatment cleans and removes moisture, chloride and other elements that may need to be sequestered prior to reuse. Cuttings have been used to stabilize road and drilling pad surfaces prone to erosion.

Packaging	50 pound bags, 1 ton totes, and bulk
Particle Sizes (mesh)	-40 or finer



Drying and solidifying cuttings



Roughnecks making connection¹

- Environmentally safe and in most cases treated cuttings can be disposed of at the drill location.
- Replaces fly ash (which may be banned by the EPA), LKD, and other hazardous ingredients.
- Requires less BRZ™ than fly ash, etc.
- Can be mixed in half tanks or with other equipment similar to current practices from sand traps in the mud banks or from cyclones.
- Sequesters heavy metals and radioactive metals into the lattice of BRZ™ where they are not water soluble.
- Sequesters sodium, barium and other elements into the lattice of BRZ™ where they are not water soluble.
- BRZ™ is a natural pozzolan (cementitious product) that molds to the form but remains pliable. BRZ™ can be combined with cuttings and 10-20% lime to be used as a concrete that is of high compressive strength and resistant to salt and underwater corrosion. It will encapsulate everything it has absorbed.



Injection well

1. Roughneck image source: Hawai'i Groundwater & Geothermal Resources Center, University of Hawai'i at Mānoa: <https://www.higp.hawaii.edu/hggrc/gallery/true-mid-pacific-rig-workers-drill-site-equipment/>

PRODUCED WATER AND FLOWBACK WATER



Produced water and frac flowback

Packaging	50 pound bags, 1 ton totes, and bulk
Particle Sizes (mesh)	-40 or finer

APPLICATIONS

Treating and reusing produced waste water with low-cost BRZ™ can offset disposal costs and increase water availability as fresh water sources become more limited and controlled. BRZ™ is used as a filter media for drinking water, storm water, and for cation removal. Frac flowback contains between 8-10% salt. BRZ™ can be used to filter produced water for injection reuse and sequester salt and other elements prior to disposal.

SURFACE MODIFIED BRZ™ (SMZ)

APPLICATION

- Surface modifying BRZ™ with a quaternary amine allows it to collect benzene, toluene, ethylene and xylene (BTX), for effective clean up of produced water.

COAL BED METHANE (CBM) GAS PRODUCED WATER

The United States reserve of natural gas from CBM is huge, with approximately 13% underlain with coal.

CMB gas production starts by drilling a series of holes into the coal seam to relieve the hydrostatic pressure that holds the gas in the seam. Submersible water pumps or artesian pressure are used to lift the water. Initially, CBM wells produce a tremendous volume of water during the unloading stage. Produced water drops off dramatically during the life of the well as gas production comes in. CBM gas well production is high water and low gas volume in the beginning, followed by increased gas flow and lower water.

The largest obstacle to the industry is the management of produced water which is contaminated with high levels of sodium. About 50% of hydraulic fracturing fluid (flowback and produced water) is stored in surface ponds and allowed to evaporate until it can be disposed of. The estimated cost to dispose of water from a hydraulic fracked well over a 20 year life cycle is estimated at \$160 million, including trucking, water disposal fees and labor.

Deep-well underground injection is also used to dispose of fracking fluids but attention to groundwater contamination is increasing leading Pennsylvania to outlaw it as a disposal method. Other states will most likely follow with restrictions in the future.

Water treatment becomes the only viable option to injection or evaporation. The sodium adsorption ratio (SAR) is often used as the discharge criteria and is expressed in molar equivalents:

$$SAR = \sqrt{\frac{Na}{Ca + Mg}}$$

The SAR should typically be in the range of 8 to 12 in the Powder River Basin, Wyoming for surface discharge. On the other hand water with TDS of less than 4,000 ppm is considered non-saline.

CATION EXCHANGE PROCESS

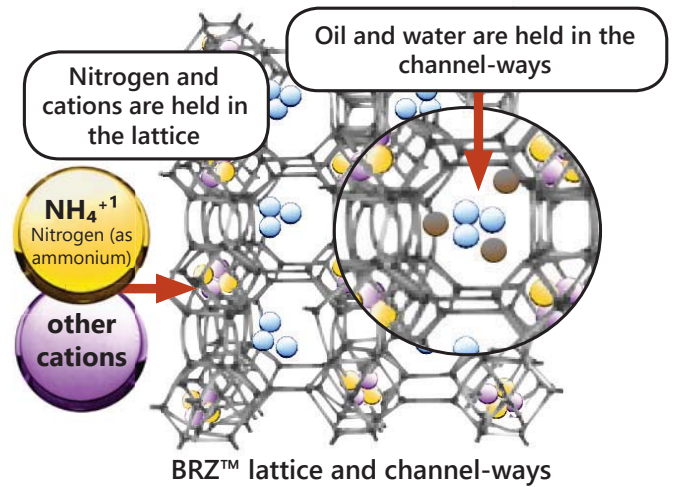
BRZ™ has two ways of holding cations (positive ions; such as sodium).

The first way is in its crystal lattice where the ammonium and other cations are held and are not water soluble.

The second way is in its channel-ways, where BRZ™ can hold up to 55% of its weight in water. In this case the cations are more loosely held and are water-soluble. BRZ™ is an excellent desiccant.



Injection well paper filter containers



CATION AND ANION REMOVAL

Radium removal

BRZ™ can be used to filter radioactive radium from flowback water before injection or to encapsulate radioactive paper filter media from used filters.

Cation Removal

BRZ™ is a negatively charged cation exchange agent. As a result of its high cation exchange capacity, BRZ™ is able to exchange various cations (ions with a positive charge) into its lattice depending on their molecular size, competing cations, and concentrations. During the cation exchange process, cations move from the BRZ™ mineral lattice and are replaced by other cations, which are held in a non-water soluble state within the lattice.

Anion Removal

Bear River SMZ (surface modified zeolite) is also available for anion removal. The negative surface charge of BRZ™ is modified to a positive charge, which allows the exchange of anions (ions with a negative charge) into the lattice. The alteration in charge allows the mineral to remove anions, such as bicarbonates (HCO_3^{-1}), carbonates (CO_3^{-2}), sulphates (SO_4^{-2}), sulfites (SO_3^{-2}), chlorides (Cl^{-1}) arsenates (As^{-1}), nitrates (NO_3^{-1}), nitrites (NO_2^{-1}) and phosphates (PO_4^{-3}).

Partial list of Cations Removed by BRZ™

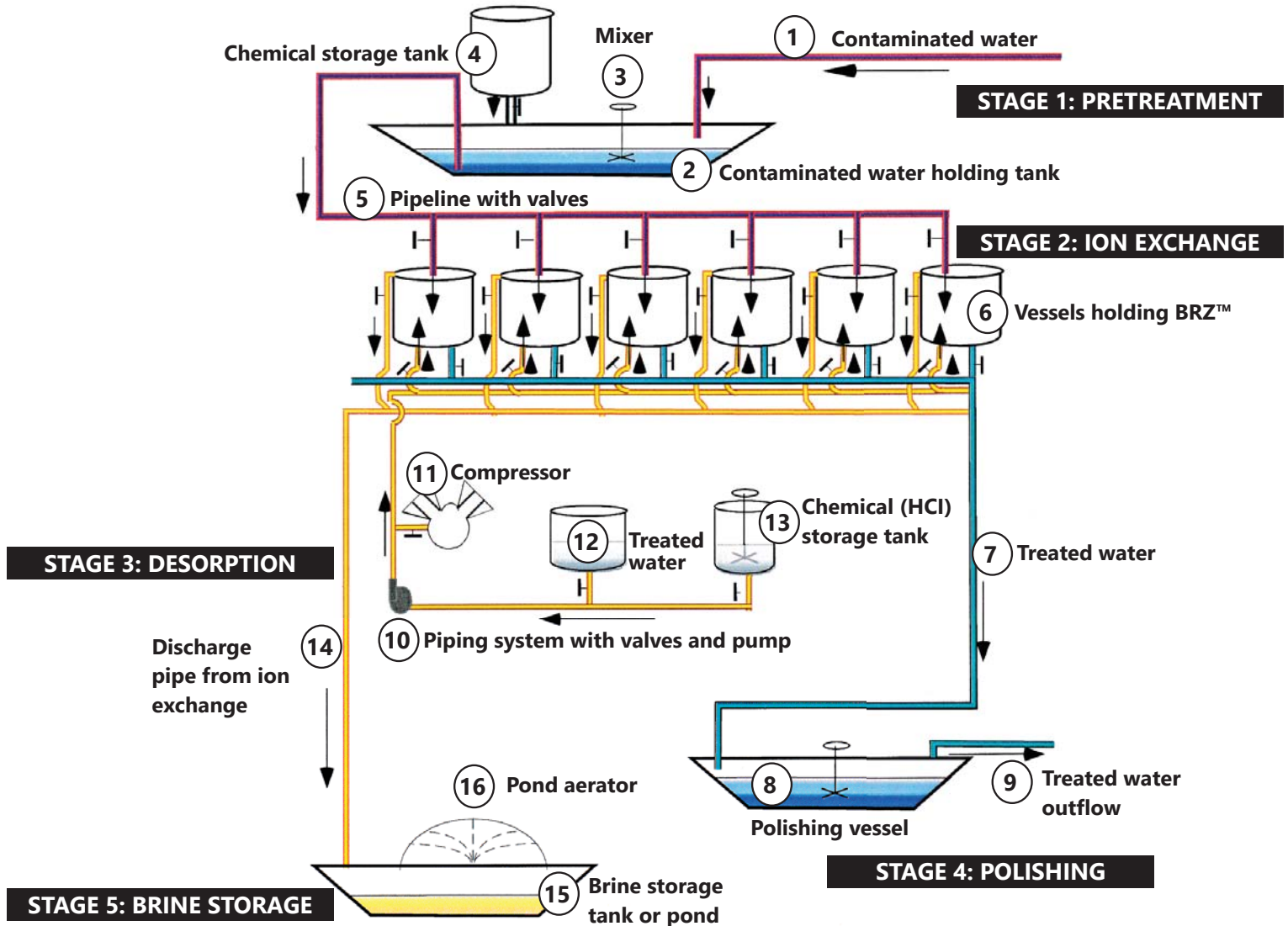
Radicals	Heavy Metals	Light Metals	Radioactive Elements
Ammonium NH_4	Lead Pb	Sodium Na	Radium Ra
	Zinc Zn	Potassium K	Uranium U
	Cadmium Cd	Calcium Ca	Strontium Sr
	Copper Cu	Aluminum Al	Cesium Cs
	Iron Fe	Magnesium Mg	
	Manganese Mn		
	Antimony Sb		
	Mercury Hg		
	Nickel Ni		
	Cobalt Co		
	Beryllium Be		
	Zirconium Zr		
	Arsenic As		
	Chromium Cr		
	Thallium Tl		
	Rubidium Rb		
	Silver Ag		
	Barium Ba		
	Selenium Se		
	Molybdenum Mo		

TREATMENT FOR CBM AND OIL WELL PRODUCED WATER

BRZ™ has a very low sodium content (less than 0.5% that is non-soluble), a high cation exchange capacity, allowing it to exchange 40 to 60 pounds of sodium per ton of BRZ™. It is resilient and has very low impurities that would cause break down in an exchange bed. Depending on the parameters of the water to be treated, the steps may include:

1. **PRETREATMENT:** An option when TDS level is high, such as in Eastern basins
2. **CLARIFICATION:** Processed in a standard thickener
3. **EXCHANGING:** Running the water through a bed of BRZ™
4. **DESORPTION:** When BRZ™ is loaded to capacity with sodium and/or other cations it can be desorbed with another cation, such as magnesium sulfate or ammonium sulfate, and reused. During the desorption cycle, the desorbed brine must be sequestered and disposed of in an ejection well, disposed of at a hazardous materials facility or allowed to evaporate in a holding pond. Resulting salt left after evaporation can be sold.

ION EXCHANGE FLOW DIAGRAM



ION EXCHANGE FLOW PROCESS

STAGE 1	Incoming contaminated water enters the holding tank for storage, homogenizing, and pretreatment for problematic cations, anions, gases, and particulates. Water is agitated and treated with chemicals.
STAGE 2	Pretreated water is processed in ion exchange vessels, treated with hydrochloric acid and rinsed.
STAGE 3	Desorption of chemicals from treated effluent.
STAGE 4	Final chemical adjustment and aeration then discharge to a river, irrigation system, etc.
STAGE 5	Effluent enters brine storage vessel or lined earthen dam for further concentration of sodium by aeration.

OIL SPILL AND BLOWOUT REMEDIATION



BRZ™
the only
way to fly



Oil soaked pelican



On shore oil spill



Off shore oil spill

Size	-40 mesh or as fine as 20-25 microns
Surface Area	24.9 Square meters per gram
Oil capacity	Absorbs up to 30% of its weight in oil

APPLICATIONS

OIL SPILLS ON WATER SURFACE

- Use for reserve pit, pond, river and off shore oil spills and coastal boundaries.
- Apply as a dust on the surface of water that has an oil-sheen.
- Apply from aircraft or from vessels.
- Disperse as a dust by disc distributors, pneumatic-venturi guns, or many other methods.



Aerial application



Pneumatic-venturi gun

Process:

1. When BRZ™ is surface applied to water to remove oil sheen, the dry dust floats due to the air in the numerous channelways in the mineral.
2. The floating mineral absorbs the oil and the specific gravity of the mineral increases. At a saturated level, the mineral coagulates into clumps and sinks.
3. Depending on the thoroughness of the mixing, BRZ™ will hold the oil indefinitely on the sea floor or bottom. In the case of an oil-sheen, all the oil enters the mineral channel-ways and is permanently encapsulated after it sinks.
4. In the case of massive amounts of oil, the oil will initially sink when absorbed by BRZ™. Larger globules are released back to the surface and will be contained by additional BRZ™ treatment.
5. BRZ™ can be inoculated with oil digesting microbes.



BRZ™ applied to oil on the surface of water



Oil held in BRZ™ is absorbed



BRZ™ holding oil sinks



Oil held in BRZ™ (settled on the bottom)

BLOWOUTS

- Absorb hydrocarbons from blowouts by covering with BRZ™.
- Booms and bats can be filled with BRZ™ to contain the spill.
- Clean vegetation with BRZ™.
- Bird and waterfowl can be safely cleaned with BRZ™.



Off shore blowout



Reclamation booms on beach

HYDROGEN SULFIDE CONTROL

APPLICATIONS

- Hydrogen sulfide gas is a health hazard and it generates sulfurous and sulfuric acid that corrodes iron and ruins office and laboratory equipment. BRZ™ is impregnated with potassium permanganate that oxidizes hydrogen sulfide in the air filter. The sulfur dioxide can then be precipitated into the BRZ™ with iron or a compound of iron for complete removal.
- BRZ™ is also a very effective volatile organic vapor (VOC) absorbent that is used in filters in oil and gas refineries and on the vents of storage tanks for hydrocarbons.



Refinery

PRESSURE SWING APPARATUS (PSA)

APPLICATION

- A PSA using clinoptilolite removed nitrogen from landfill gas and also from natural gas.

TREATMENT OF HIGH SALINITY SOILS

INTRODUCTION

High salinity, sodic, and saline-sodic soils are worth very little or nothing. Other than oil and gas or mineral rights, the land is generally worthless.



Sodic soil

SALINE SOIL PROBLEMS

- Soil salinity problems generally occur in semiarid or arid areas where there is not enough meteoric water to leach salts from the root zone of the plants.
- Saline soils may be reclaimed by providing good percolation, drainage, and good quality water to leach the salts.
- Saline-sodic soils behave differently than sodic soils and have different reclamation procedures.
- A saline soil is one in which there is an excess of soluble salts of calcium, magnesium, potassium, and sodium. They are generally sulfates, bicarbonates, or chlorides.
- Saline soils are a result of irrigating with high salinity water, a lowering water table that fails to leach the salts, surface migration of salts through a combination of capillary action and osmotic pressure from underlying saline deposits or soils, and evaporation of saline water bodies.
- When the concentration of salts in the soil solution equals or exceeds the osmotic concentration in the plant cells, water uptake is stopped and water moves out of the cells to create plasmolysis or "burning."
- Plants are more sensitive to high salinity during their germination and seedling stages than during later stages when they develop some immunity.
- Soil salinity measures all the ions in the soil (not just sodium), and it is measured by electrical conductivity (EC). The more the ions, the higher the salinity. It is measured in milliMhos (mmhos) per centimeter or millisiemens (mS) per centimeter. Some laboratories report it as milliequivalents per liter (meq/L). Cations are measured as milligrams in the laboratory and converted to milliequivalents to put the cations on an equal basis. The EC values in mmhos/cm or mS/cm are interpreted as follows:

EC LEVEL	PROBLEM
Below 2	No salinity problem
2-4	Restricts growth of sensitive crops
4-8	Restricts growth of many crops
8-16	Restricts growth of all but salt tolerant crops
Above 16	Only a few very tolerant crops make satisfactory yield

SODIC SOIL PROBLEMS

- When the percentage of sodium exceeds 15% of the cation exchange capacity of the soil, the soil is considered "sodic." The sodic condition retards or stops plant growth.
- Sodium, chloride, and boron are toxic ions for plants. Plants may display toxicity symptoms before they are effected by high salt concentrations.
- Sodium is generally toxic to plants at higher concentrations. The main problem with sodium is that it attaches to and disperses clays to restrict percolation.
- Soils with a high accumulation of sodium are characterized by having poor tilth and low permeability making them unfavorable for plant growth. When there is a high concentration of sodium, the ionic sodium attaches to clay particles and causes them to disperse and the permeability of the soil becomes very low.
- Sodic soils can be remediated by the application of gypsum or sulfur. In the case of gypsum, soluble calcium is provided to displace the sodium from the clay and to solubilize the sodium as sodium sulfate. In the case of elemental sulfur, there must be a reserve of free lime (calcium carbonate). The sulfur as a result of bacterial action forms sulfuric acid that attacks the calcium carbonate to provide calcium to displace the sodium from the clay, and solubilize the sodium as sodium sulfate. Generally, if the calcium carbonate content of the soil is less than 1.5% gypsum should be used; if the calcium carbonate content is between 1.5% and 2.5% either gypsum or sulfur can be used; and when the calcium carbonate content is greater than 2.5% sulfur is recommended. Again, the success of these amendments depend on the application of clean water.
- A sodic problem should be corrected prior to seeding.
- Plant growth is important for erosion control and phytoremediation (metals uptake)



Pump and high salinity field

SALINE-SODIC SOIL PROBLEMS

- Land application of produced water from conventional natural gas wells and coal bed methane gas wells has produced both sodic and saline soils.
- In the case of saline-sodic soils, it is likely that physical soil problems caused by the sodium (attaching to clays) restrict the leaching of the salts. This can be a significant problem even in wetter climates. Saline soils can be reclaimed in semi-arid and arid climates under the right conditions.

APPROACH TO PROBLEM

We will assume that water is not available due to the cost of irrigating, the fact that it is an arid area with little rainfall, or the possibility that the well or surface water is saline. This excludes the approach of decreasing the salinity by leaching. The lack of water also preempts the reduction of the sodium by applying gypsum or sulfur.

This scenario leaves another approach: to decrease the content of the salt by applying a cation exchange amendment to absorb the sodium and allow the germination and seedling growth of salt tolerant species. To test this theory, a Canadian group spread a layer one eighth to one quarter of an inch thick of a 30% clinoptilolite product over the soil. At one eighth inch this would amount to 12 tons per acre (tpa), and this application rate would only be economic for a very limited market. What grass was available grew very well. A 90% plus clinoptilolite product such as BRZ™ should reduce the amount of zeolite used. Hopefully the application rate could be cut to 2.5 to 6 tpa depending on the amount of the salinity.

PROPOSED TEST

A sodic area should be mapped into a 10 foot by 10-foot square grid using steel rebar posts. At least three replicates of each test should be planted. The tests should include varying amounts of zeolite, perhaps 2.5, 5, and 7.5 tpa top-dressed. Additional testing options could include:

- Simultaneous and delayed seeding
- Areas where native grasses are already established but are doing poorly
- Typical crops currently being used in surrounding areas such as canola, corn, wheat, barley, timothy, or brome
- Testing of some of the alkali-adapted species (in the table below)

Inland salt grass	Alkali grass	Hordeum brachyantherum
Newhy hybrid wheatgrass	Nuttall alkaligrass	Elymus triticoides
Tall fescue	Tall wheatgrass	Agropyron smithii
Meadow barley	Distichlis spicata	Puccinellia distans
Creeping wildrye	Agropyron hoffmannii	Puccinellia nuttaliana
Western wheatgrass	Festuca arundinacea	Agropyron elongatum

CONCLUSIONS

While the proposed process is the result of physical activities, the reactions are still largely chemical. The calcium and potassium from the Amended BRZ™ will exchange with the sodium in the sodic soil. In order for the process to continue, the sodium forced off of the exchange process becomes “soluble” sodium rather than “exchangeable” sodium and some leaching of the sodium must still be accomplished for the exchange to continue. The efficiency of this process will be governed by a number of factors including the soil particle size or texture, natural and man-made salt content of the soil, Amended BRZ™ size and application rate, and the availability of water. Remediation can be accomplished in semi-arid and arid climates.

Soils high in clay content are most adversely affected by the presence of sodium and salts. Sodium only has effects on soil clays. Soils that are sandy are largely unaffected by sodium. High clay content soils are difficult to leach salts through even in the absence of sodium. The addition of Amended BRZ™ will help ameliorate the effects of high clay content.

Sodium in the absence of significant salts, causes clays to swell and/or disperse and translocate through the soil profile. If only swelling has occurred, the effects of high sodium are reversible. Dispersion and translocation of clays due to sodium are generally irreversible. Salts have a negative impact on soils. However, salts tend to flocculate soil clays and negate the swelling and dispersion. The key is to balance the level of salts so that they do not become a toxic issue.

The application rate for the zeolites can be calculated on both a chemical and physical basis. Application rates should be based on a cation exchange goal. Knowing the sodium level of the soils and the exchangeable calcium, magnesium, and potassium level of the zeolite allows for the calculation of the amount of zeolite needed. Testing is very important in determining the best size fraction and application rates for the zeolite in relation to improving the soil hydraulic properties in addition to allowing for the most efficient chemical exchange.



Pump in poppy field