BEAR RIVER ZEOLITE BRZ™

NUCLEAR REMEDIATION

Bear River Zeolite (BRZ™) is a natural volcanic origin rock called "clinoptilolite" that is one of over 40 zeolite minerals. BRZ™ is used for water filtration, cation removal, and has also been used successfully for nuclear remediation.

HIGH QUALITY MEDIA

- ✓ High cation exchange capacity (CEC) up to 220 meq/100 g
- ✓ High 85-95% clinoptilolite content
- ✓ Adsorbs up to 55% of its weight in water
- ✓ Durable with a hardness of 3 on Moh's scale
- ✓ pH of 8.64
- ✓ Low sodium content of <0.5% (which is insoluble)
- ✓ High potassium content of 2.93 to 3.47%
- ✓ Low clay content
- ✓ Surface area of 24.9 square meters/gram
- ✓ Low cost and readily available

Remediation Treatment Methods

CATION EXCHANGE

BRZ™ has a high aluminum (Al^{3+}) clinoptilolite framework, giving it a negative charge that captures and holds multiple cations and radioactive isotopes through cation exchange.

Ca, K, and Na are released from its lattice in exchange for radioactive isotopes and various cations (figures 1 & 2) depending on their molecular size, competing cations, and concentrations. The radioactive isotopes and cations are exchanged into the lattice where they are not water soluble.

Figure 2 **CATIONS**

RADICALS

NH^4 Ammonium

HEAVY METALS

Pb Lead	**Zn** Zinc	**Cd** Cadmium	**Cu** Copper	**Fe** Iron
Be Beryllium	**Zr** Zirconium	**As** Arsenic	**Cr** Chromium	**Tl** Thallium
Mn Manganese	**Sb** Antimony	**Hg** Mercury	**Ni** Nickel	**Co** Cobalt
Rb Rubidium	**Ag** Silver	**Ba** Barium	**Se** Selenium	**Mo** Molybdenum

LIGHT METALS

Na Sodium	**K** Potassium	**Ca** Calcium	**Al** Aluminum	**Mg** Magnesium

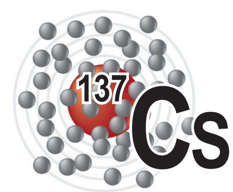


Figure 1 **RADIOACTIVE ISOTOPES**

ELEMENT	ISOTOPE	HALF LIFE
^{90}Sr	Strontium	28.8 years
^{137}Cs	Cesium	30.17 years
^{235}U	Uranium	703.8 million yrs
^{238}U	Uranium	4.468 billion yrs
^{233}U	Uranium	160,000 yrs
^{226}Ra	Radium	1,600 yrs
^{232}Th	Thorium	14.05 billion yrs
^{87}Rb	Rubidium	49 billion yrs
^{89}Rb	Rubidium	15.15 minutes
^{129}I	Iodine	15.7 million yrs
^{131}I	Iodine	8 days

SURFACE MODIFIED ZEOLITE (SMZ)

The surface charge of BRZ™ can be modified to a positive charge to exchange anions (figure 3). The modifier is typically a quaternary amine.

Figure 3 **ANIONS**

HCO_3^{-1} Bicarbonates	**CO_3^{-2}** Carbonates	**SO_4^{-2}** Sulphates
SO_3^{-1} Sulfites	**CL^{-1}** Chlorides	**As^{-1}** Arsenates
NO_3^{-1} Nitrates	**NO_2^{-1}** Nitrites	**PO_4^{-3}** Nitrates

In field research using BRZ™ to remediate ^{90}Sr groundwater contamination

West Valley Demonstration Project

A Permeable Treatment Wall using BRZ™ to Remove ^{90}Sr from groundwater

In 2010 the West Valley Demonstration Project (WVDP) developed the first full-scale Permeable Treatment Wall (PTW) to remediate and contain a ^{90}Sr contaminated groundwater plume. The source of ^{90}Sr was identified as a leak in a process line from 1968 to 1971. The radioactive contamination created an underground plume that had been slowly migrating over 30 years. Chamberlain, et al, 2011

BRZ™ was selected for the project based on comparison testing with the clinoptilolite used in a Wall-and-Curtain PRB installed at Chalk River, Ontario in 1998. BRZ™ had a higher CEC, was harder and had minimal clay content. The PTW is approximately 259 meters (860 feet) long, 5.8 – 9.1 meters (19-30 feet) deep and contains 2,600 metric tons of BRZ™. Seneca & Rabideau, 2012

BRZ™ removes ^{90}Sr by ion exchange as plume groundwater passes through the PTW wall. Two downgradient monitoring wells illustrate reduction levels (figures 4 & 5). The PTW has minimized the expansion of the plume and decreased ^{90}Sr in groundwater (figure 6). Steiner, 2018, CH2M HILL BWXT West Valley, LLC, 2018

PTW construction at WVDP
Reprinted with permission from Alan Rabideau, University of Buffalo, Buffalo, NY.

Figure 4 **^{90}Sr Concentrations well MW-28-SWS**

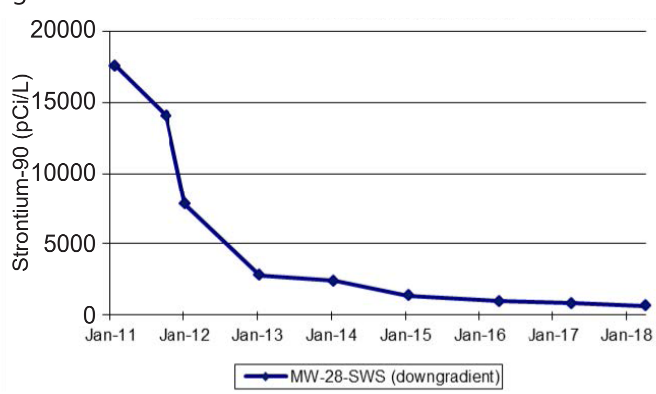
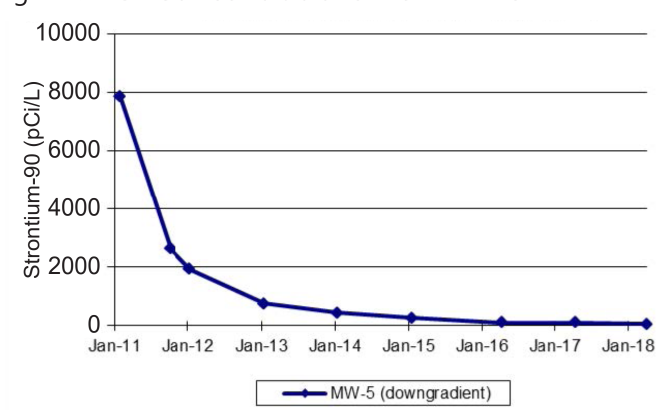
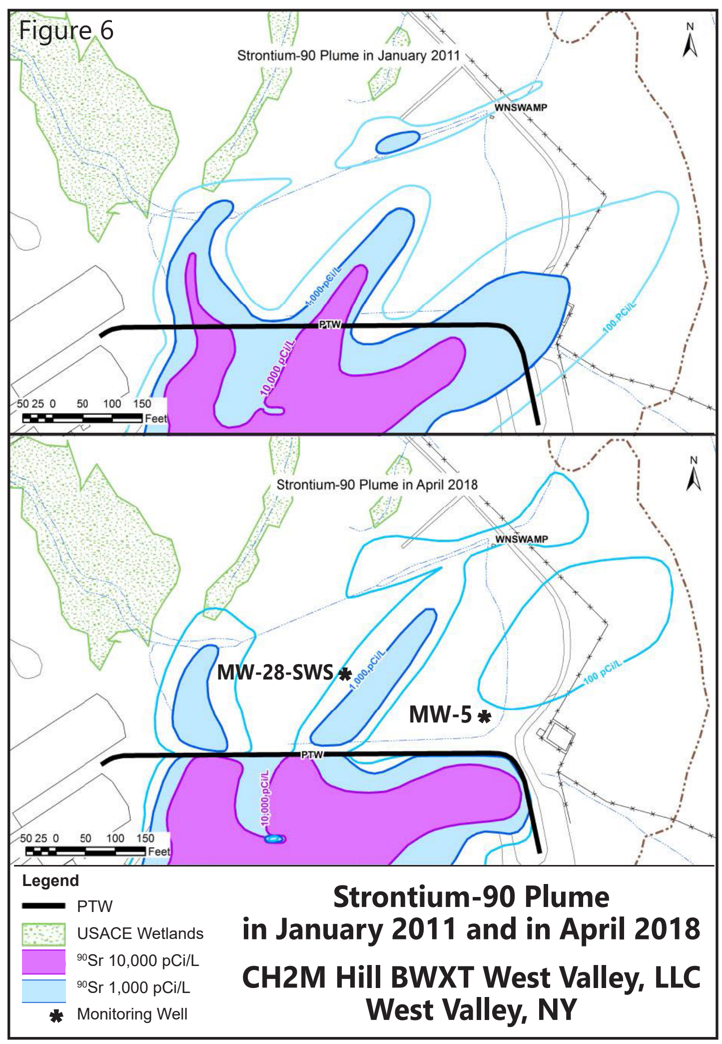


Figure 5 **^{90}Sr Concentrations well MW-5**



Figures 4 - 6 Adapted from Steiner, B. 2018. As presented to the West Valley Citizens Task Force.



Chalk River Laboratories (CRL) Waste Management Area

A Funnel and Gate Permeable Reactive Barrier (PRB) using BRZ™ to manage and halt a groundwater plume contaminated with ^{90}Sr

A major nuclear reactor accident occurred at Atomic Energy of Canada Ltd, Chalk River, Ontario in 1952. [Wikipedia] A pilot plant was installed in an attempt to remediate water contaminated with ammonium nitrate and mixed fission products resulting from the event. Monitoring in the 1990's identified ^{90}Sr groundwater contamination in a 400 meter (437 yards) long aquifer section, creating an underground plume that was migrating toward wetland.

Chalk River Nuclear Laboratories

Chalk River Laboratories (CRL) installed a Wall-and-Curtain Permeable Reactive Barrier (PRB) in 1998 to remediate the ^{90}Sr groundwater contamination and slow or halt its spread to the wetland. The Wall-and-Curtain PRB construction included a 28 meter steel sheet barrier wall with an 11 meter wide, 2 meter thick curtain that held 118 cubic meters of clinoptilolite. The clinoptilolite used in the Wall-and-Curtain PRB had a CEC of 165 meq/100 g, contained clay and was found to be friable, which affected hydraulic conductivity. [Lee and Hartwig, 2001, Seneca & Rabideau, 2012, Hoppe, 2012, Gillespie, 2016]

A second Funnel-and-Gate PRB wall was installed in 2013 at the CRL Waste Management Area A (WMA A). The WMA A is a radioactive waste storage site with waste stored in unlined shallow sand trenches, concrete bunkers, and direct to ground burials as interim solutions to permanent disposal. The WMA A is located in sandy soil above the groundwater table and has leached ^{90}Sr downhill. The ^{90}Sr contaminated groundwater plume discharges into the South Swamp watershed, which flows into Perch Lake and ends up in the Ottawa River.

The Funnel-and-Gate PRB wall was installed to contain the plume and prevent further ^{90}Sr contamination. The PRB has three gates that are filled with BRZ™, which was selected to increase ^{90}Sr removal and improve hydraulic conductivity. Sheet piling between the gates creates a funnel to guide groundwater to the gates. ^{90}Sr is exchanged into the BRZ™ lattice as contaminated water passes through the gates. The gates are 8.5m to 9.9m deep, 3m thick and vary in length.

- West Gate: 9.42 meters
- Central Gate: 10.77 meters
- East Gate: 12.11 meters

Results from a 14 month sampling period indicate the Funnel-and-Gate PRB wall removed high levels of ^{90}Sr. (figure 7). Monitoring has shown the PRB has reduced ^{90}Sr concentrations in downgradient effluent groundwater when compared to upgradient influent. [Canadian Nuclear Laboratories, 2019]

Figure 7 **Chalk River PRB 14 Month Sampling Period** [Adapted from Gillespie, 2016]

GATE	^{90}Sr Removal	Remaining ^{90}Sr in effluent	Other Effluent Changes Observed when compared to influent
WEST	>98%	10 Bq/L	Ca & K 5 times higher, 30% decrease in Na
CENTRAL	>99%	2 Bq/L	Ca, K & Na increased significantly
EAST	approx. 92%	1 Bq/L	Ca, K & Na twice as high

[1 becquerel (Bq) = 1 disintegration per second (dps)] [Berkeley Lab]

REMEDIATION APPLICATIONS

Permeable Treatment Walls (PTWs) and Permeable Reactive Barriers (PRBs)

PTWs and PRBs should be installed with 14 x 40 mesh BRZ™ downstream from the source of contamination to stop the migration and release of contaminated groundwater. A series of reactive barriers or treatment walls could be used at sites where multiple contaminants are present. The combination of fill media selected for specific contaminant removal could increase remediation efficiencies. [ITRC, 2011]

Pump Back System

Drill pump back wells could be installed downstream of nuclear sites where migrating contaminated groundwater is too deep to treat with a PTW. The contaminated water would be pumped back upgradient and filtered through a gravity bed or pressure filter containing 14 x 40 mesh BRZ™.

Encapsulation of Nuclear Waste

BRZ™ can be mixed with Portland cement and contaminated material to encapsulate nuclear waste prior to HAZMAT storage. BRZ™ is a very effective Pozzolan.

Vitrification

BRZ™ is a high silicate media that could be used to vitrify radioactive waste into glass. The process involves mixing radioactive waste with BRZ™ and heating it to 1100 degrees centigrade or higher. The outside cools faster with the radioactive materials the last to cool, which forces them to the center where they are encapsulated in a thick layer of glass.

Drill Hole Fence and Floor

A reactive barrier could be constructed by drilling a series of holes in the form of a fence and fracing them with BRZ™ as a frac media. A floor could also be installed by horizontal drilling, fracing and using BRZ™ as the frac media. Horizontal drilling has been suggested as an option to capture contaminants under structures and buildings.[ITRC2011]

Reactive Sandpacks for In-Situ Treatment of Construction Dewatering Effluent

A research study developed reactive sandpacks as a cost effective alternative to current methods for effluent storage, testing and decontamination. Sandpacks filled with clinoptilolite could be placed underground around dewatering wells to treat contaminated water in place prior to surface release. [Priebe. and Lee, 2013]

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*Data on file at Bear River Zeolite Co.