SAND2016-3010PE

Formation of Permeable Reactive Barriers (PRB) for Heavy Metals and Radionuclides Using an Apatite Forming Solution

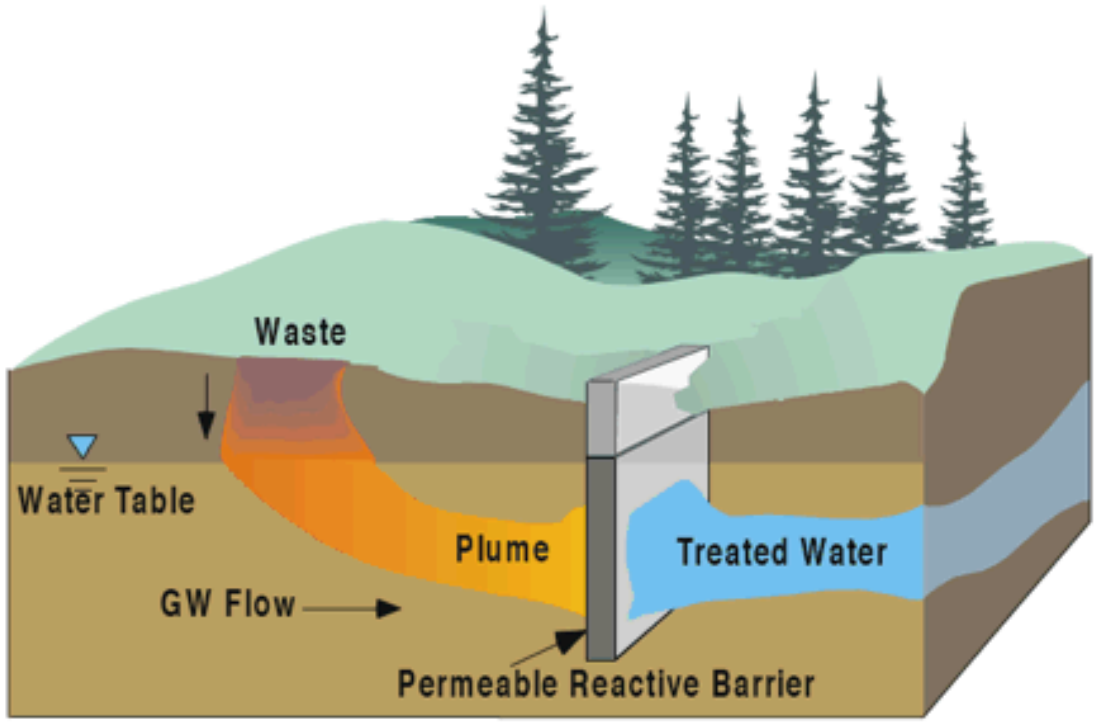
Presented to the New Mexico Chapter of the Air & Waste Management Association

Robert Moore and Mark Rigali
Sandia National Laboratories
April 5th, 2016

Topics to Be Covered

- Permeable Reactive Barriers
- The DOE Hanford Site – Specifically the 100N Site
- The Problem at the 100N site
- The Solution – An injectable solution for the formation of apatite in sediment to construct a permeable reactive barrier.
- Summary

Permeable Reactive Barriers



Contaminated groundwater flows through the reactive barrier where the reactive media removes or destroys the contaminant and treated, contaminant free groundwater exits the barrier.

Conventional Permeable Reactive Barrier Construction

Trenching Followed by Backfilling with a Reactive Media

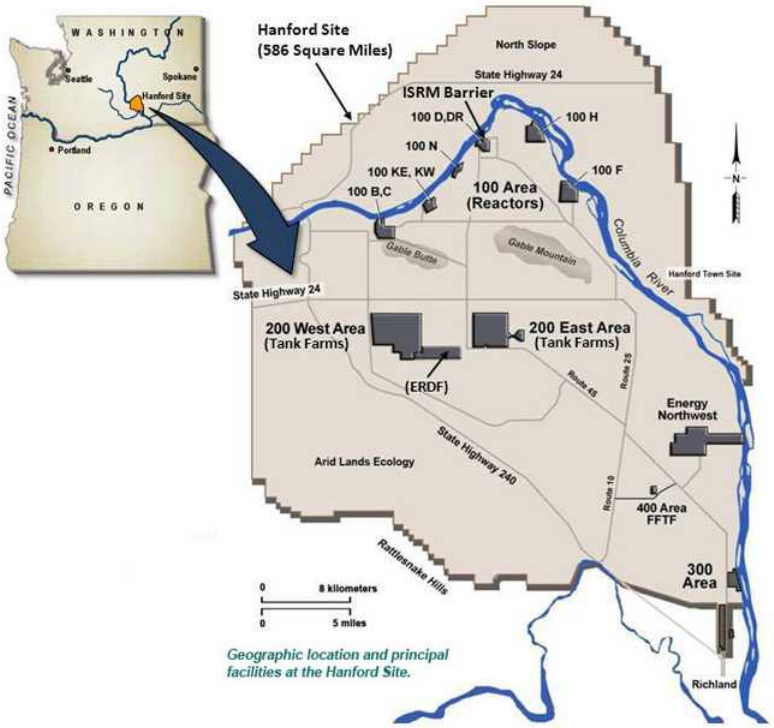
Jet or Grout Injection of A Reactive Media

Challenges With Conventional Construction Methods for PRBs

- Typically limited to shallow depths.
- Difficult in areas with large boulders or other obstructions.
- Can change the permeability of the soil resulting in groundwater bypassing the PRB.
- Exposes workers to contaminants and risk of injury.
- Implementation under leaking tanks, piping systems, etc. can be challenging?
- Can be expensive for treatment of large areas.

The DOE Hanford Site

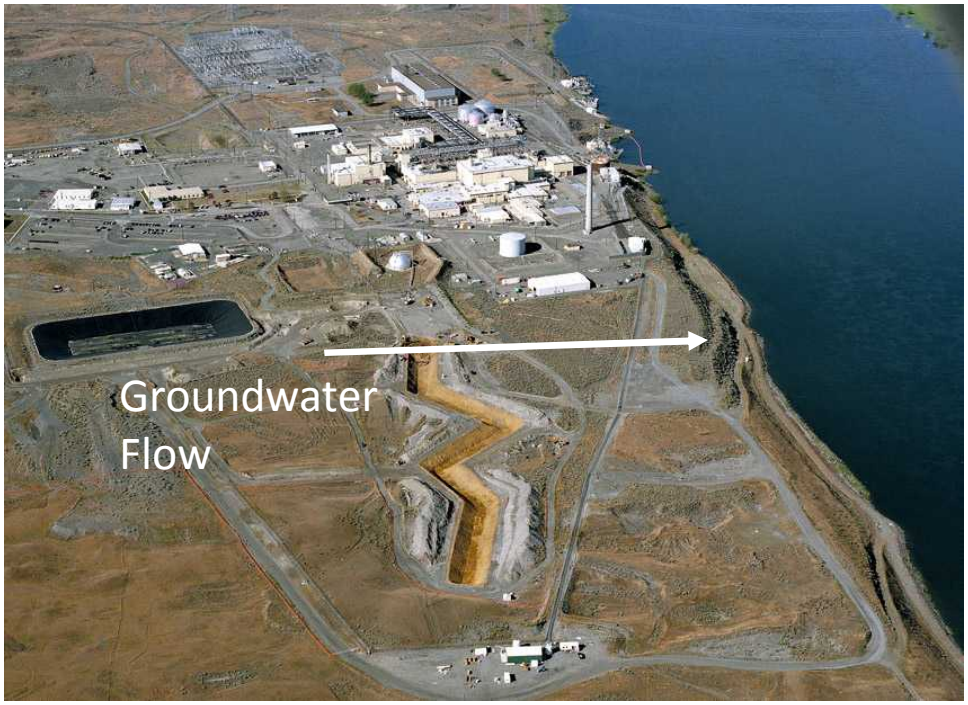
- Located in Washington State
- Former Pu production reactors and separation facilities
- Site is highly contaminated



The 100N Site on the Hanford Reservation

The Problem

- ^{90}Sr at the 100N site is entering the Columbia River.
- The area where treatment is possible contains very large boulders
- The geohydrology in the area is complex



Hanford 100N Site

Many Remediation Technologies Were Considered and Tried at the 100N Site

- Pump and Treat
- Permeable reactive barrier constructed by jet grouting
- Freeze walls
- Funnel and gate – drive sheet metal sections into the ground directing contaminated groundwater to a treatment area.

Therefore the Subcontractor Decided on a New Strategy

- **Natural Attenuation:** dilution, dispersion, bio-degradation, irreversible sorption, and/or radioactive decay of contaminants in soils and ground waters. It causes a net reduction of contaminant toxicity and human and ecological risk, but rarely taken advantage of environmental remediation.
- In other words, do nothing. Let the ^{90}Sr go into the Columbia River.

The Sandia Solution

- Construction of a permeable reactive barrier next to the Columbia River Using using apatite as the sorbent for ^{90}Sr.
- How?
  - The construction site is right on the Columbia River.
  - The permeable reactive barrier would have to be more than 30 feet deep and eventually cover up to 1000 m of the Columbia River shoreline.
  - Many methods had already been proposed and some tried without success.
  - Conventional methods alone were not feasible.

Hydroxyapatite or Apatite

- A three dimensional lattice composed of $Ca_{10}(PO_4)_6(OH)_2$
- Found as a common mineral in the environment and as a main component of bone and teeth.
- Very stable in the environment, extremely low solubility.
- Can be used to sequester a wide variety of radionuclides, heavy metals and other contaminants through substitution into the structure (conformational change) or sorption onto the surface as metal phosphate compounds.
- High affinity for contaminants, and stability and very low solubility make apatite an ideal sorbent for immobilization of many contaminants

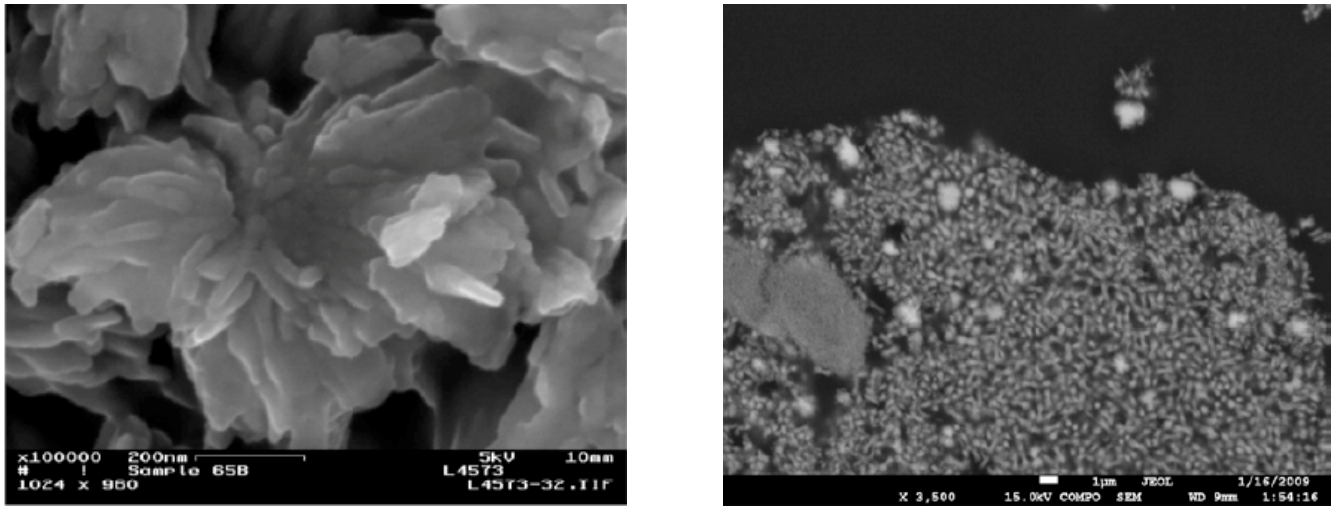
The Challenge

- How can we place a highly insoluble hydroxyapatite solid in this problematic area at 100N site?

In Situ Formation of Hydroxyapatite in Soil

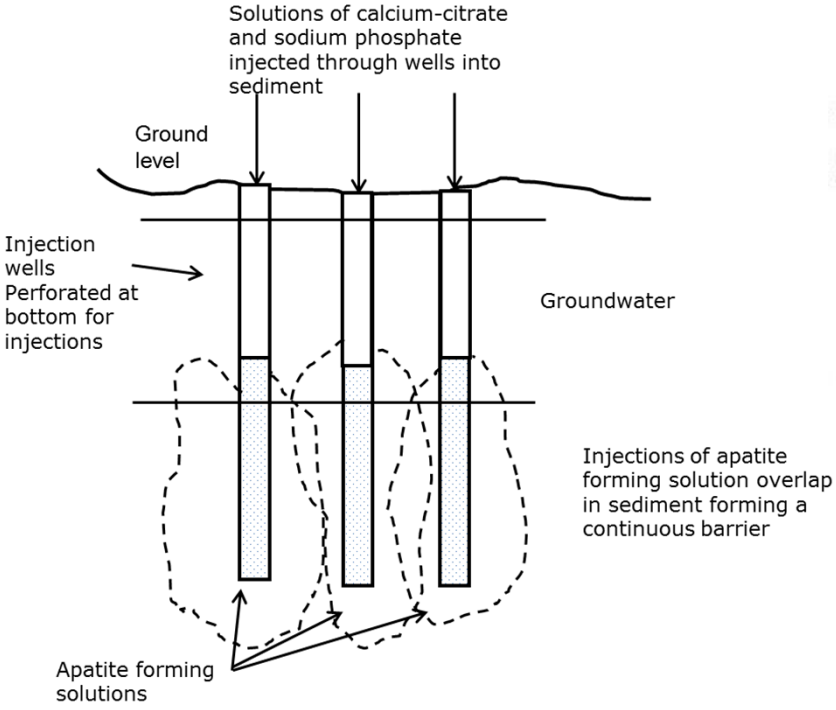
A solution of calcium-$(citrate)_2$ and sodium phosphate is stable. When placed in soil, the soil microorganisms will metabolize the citrate and release the calcium in a form that reacts with phosphate to form hydroxyapatite.

$$\text{calcium–(citrate)}_2 + \text{sodium phosphate} \xrightarrow{\text{soil microorganisms}} \text{apatite}$$

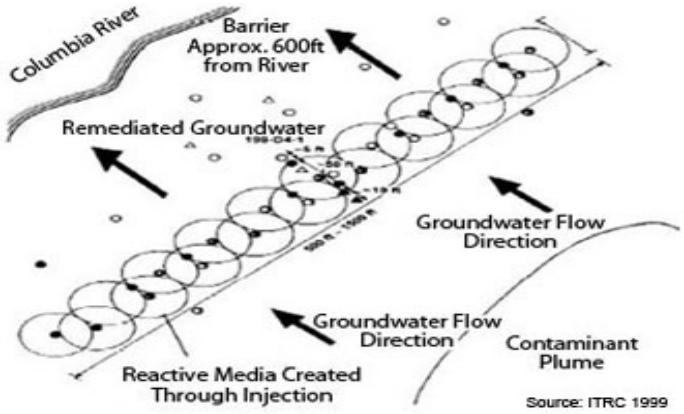


Apatite crystals formed in soil

Injections of the Apatite Forming Solution

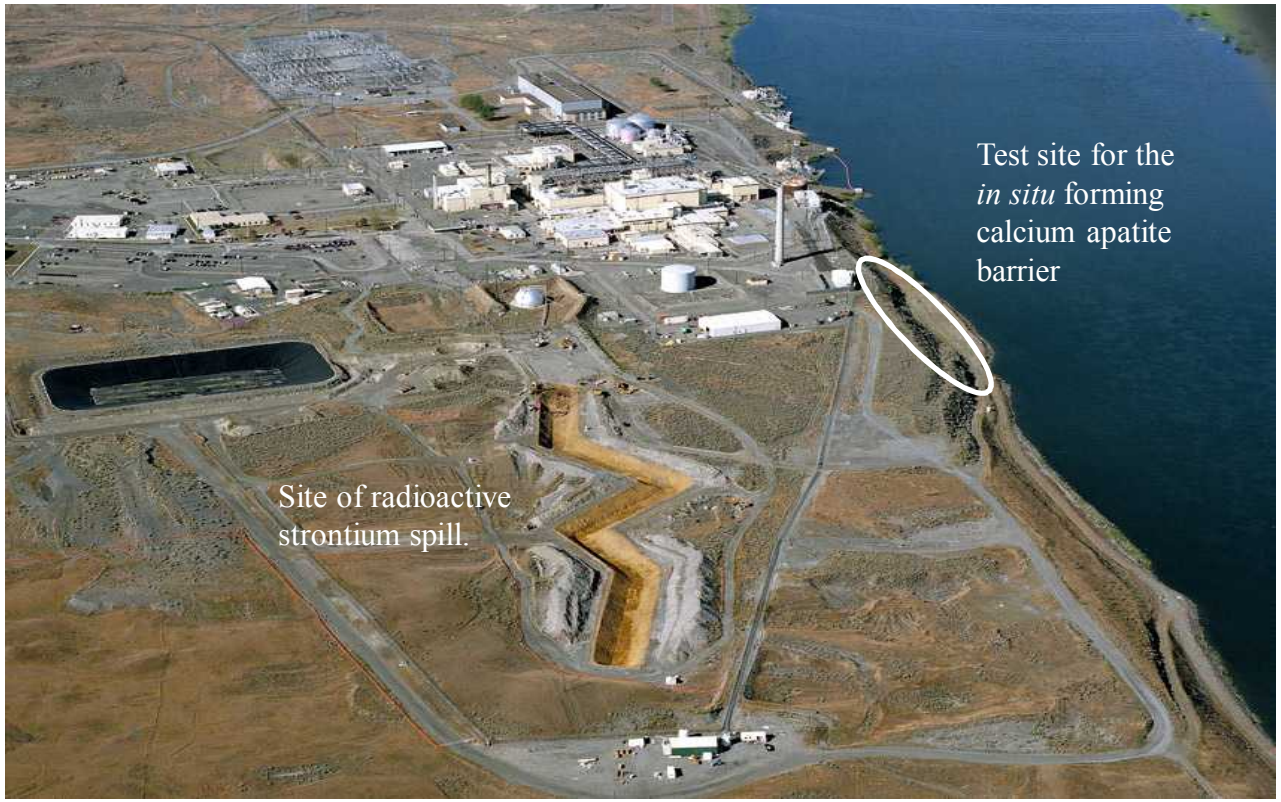


Injections of apatite forming solution overlap in sediment forming a continuous barrier



Overlapping injections of the apatite forming solution are used for construction of a continuous permeable reactive barrier

Department of Energy Hanford 100N Site, Washington State



Site for construction of the apatite barrier at the Hanford 100N Site

Shoreline at the Hanford 100N Site

Injection Well at the Hanford 100N Site

Results of the *In Situ* Formed Apatite Barrier at the Hanford 100N Site

- Initially 13 wells were placed along a 100 m section of the Columbia River and two injections of the apatite forming solution were placed in the ground.
- After approximately 1 year the barrier is sequestering between 95 and 99.99% of the ^{90}Sr.
- Sediment samples from the site have indicated the formation of strontium substituted apatite.
- Plans are in place to increase the length of the barrier to 1 km.

The Technology has Many Other Potential Applications and Significant Advantages Over Conventional Construction Methods for Permeable Reactive Barriers.

- Simple to implement and potentially less expensive than conventional methods.
- Can be used in locations where conventional methods may be challenging. i.e. – large boulders or other obstacles in the area, site is deep underground, etc.
- Minimizes exposure of construction workers to the contaminant and construction hazards
- Chemicals are not hazardous
- The barrier is easily modified. For example, additional injections can be made in the future.

The Technology has Many Other Applications

- Currently, Sandia and PNNL are evaluating the use of the barrier technology at the DOE Old Rifle Site for uranium containment.
- A variation of the apatite forming solution is being developed for use at Fukushima.

Summary

- A method has been developed and successfully deployed at the DOE Hanford Site for construction of a PRB of hydroxyapatite without extensive excavation.
- The technology can be used to sequester a wide range of radionuclides and heavy metals and has significant advantages over conventional construction methods for permeable reactive barriers.
- Currently, the technology is being evaluated for additional applications.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Thank You

Questions ?