Overview on Backfill Materials and Permeable Reactive Barriers for Nuclear Waste Disposal Facilities

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1. Introduction

A great deal of money and effort has been spent on environmental restoration during the past several decades. Significant progress has been made on improving air quality, cleaning up and preventing leaching from dumps and landfills, and improving surface water quality. However, significant challenges still exist in all of these areas. Among the more difficult and expensive environmental problems, and often the primary factor limiting closure of contaminated sites following surface restoration, is contamination of ground water. The most common technology used for remediating ground water is surface treatment where the water is pumped to the surface, treated and pumped back into the ground or released at a nearby river or lake. Although still useful for certain remediation scenarios, the limitations of pump-and-treat technologies have recently been recognized, along with the need for innovative solutions to ground-water contamination (1). Even with the current challenges we face there is a strong need to create geological repository systems for dispose of radioactive wastes containing long-lived radionuclides. The potential contamination of groundwater is a major factor in selection of a radioactive waste disposal site, design of the facility, future scenarios such as human intrusion into the repository and possible need for retrieving the radioactive material, and the use of backfills designed to keep the radionuclides immobile. (2).

One of the most promising technologies for remediation of contaminated sites and design of radioactive waste repositories is the use of permeable reactive barriers (PRBs). PRBs are constructed of reactive material(s) to intercept and remove the radionuclides from the water and decontaminate the plumes in situ. The concept of PRBs is relatively simple. The reactive material(s) is placed in the subsurface between the waste or contaminated area and the groundwater. Reactive materials used thus far in practice and research include zero valent iron, hydroxyapatite, magnesium oxide, and others. As the contaminant moves through the reactive material, the contaminant is either sorbed by the reactive material or chemically reacts with the material to form a less harmful substance. Because of the high risk associated with failure of a geological repository for nuclear waste, most nations favor a near-field multibarrier engineered system using backfill materials to prevent release of radionuclides into the surrounding groundwater.

2. Definition of a Permeable Reactive Barriers

Environmental scientists are generally familiar with the concept of barriers for restricting the movement of contaminant plumes in soil and ground water. Such barriers are typically constructed of highly impermeable emplacements of materials such as grouts, slurries, or sheet pilings to form a subsurface “wall”. The goal of such barriers is to minimize the possibility that a contaminant plume can move toward and endanger sensitive receptors, such as drinking water wells, or discharge into surface waters. Rather than serving to constrain plume migration, PRBs are designed as conduits for the contaminated ground water flow (1). As contaminated water passes through the reactive zone of the PRBs, the contaminants are either immobilized or chemically transformed to a more desirable (e.g., less toxic, more readily biodegradable, etc.) state. Therefore, a PRB is a barrier to contaminants, but not to ground-water flow. A permeable reactive subsurface barrier is defined as:

“An emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier (1)”.
3. Types of Permeable Reactive barriers

Reactive media used in permeable barriers should be compatible with the subsurface environment. That is, the media should cause no adverse chemical reactions or byproducts when reacting with constituents in the contaminant plume, and should not act as a possible source of contaminants itself. This requires that the chemistry and reactivity of the material be well understood and characterized. To keep PRB costs at a minimum, the reactive material should persist over long periods of time, i.e., it should not be readily soluble or depleted in reactivity, and the material should be readily available at a low to moderate cost. The material selected should minimize constraints on ground-water flow by not having excessively small particle size and it should not consist of a wide range of particle sizes that might result in blocked intergranular spaces (3). The table below lists various barrier types and the materials used to construct those barriers.

### Table 1. Materials used for various barrier types.

<table>
<thead>
<tr>
<th>Type of Barrier</th>
<th>Materials Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic-Sorption or Substitution Barriers – Materials that can sorb radionuclides or other contaminants.</td>
<td>Activated Alumina, Activated Carbon, Bauxite, Exchange Resins, Ferric Oxides and Oxyhydroxides, Magnetite, Peat, Humate, Lignite, Coal, Phosphates, Titanium Oxide, Zeolite (3).</td>
</tr>
<tr>
<td>Inorganic-Precipitation Barriers – Materials that cause precipitation of radionuclides or other contaminants.</td>
<td>Biota, Dithionite, Ferrous Hydroxide, Ferrous Carbonate, Ferrous Carbonate, ferrous Sulfide, hydrogen Sulfide Gas, Lime, Flyash, Limestone, Miscellaneous [Mg (OH)2, MgCO3, CaCl2, CaSO4, BaCl2], Zero-Valent Metals (3).</td>
</tr>
<tr>
<td>Inorganic-Degradation Barriers – Materials that react or change the oxidation state of radionuclides or other contaminants.</td>
<td>Biota and Zero-Valent Metals (3).</td>
</tr>
<tr>
<td>Organic-Sorption Barriers – Materials that can sorb radionuclides or other contaminants.</td>
<td>Zeolite, Activated Carbon, Clays (3).</td>
</tr>
</tbody>
</table>

4. Reactant and Reaction Mechanism of Some PRBs

4.1. Mechanisms of Uranium Interaction with Hydroxyapatite for Ground Water Remediation

Hydroxyapatite and other apatite minerals have been found effective in immobilizing lead and other metals through the formation of metal phosphates that are insoluble over a range of chemical conditions (4,5). Recently, additions of hydroxyapatite to uranium contaminated
Sediments were shown to decrease uranium solubility (6). Calcium apatite is a family of compounds with the general chemical structure $\text{Ca}_{10-n}X_n\text{(PO}_4\text{)}_{6-m}Y_mZ_2$ where $X$ and $Y$ are cation and anions, respectively that substitute for $\text{Ca}^{2+}$ and $\text{PO}_4^{3-}$ groups in the apatite structure. Typical cation substitutes include $\text{Sr}^{2+}$, $\text{Na}^+$, $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$ while anions substitutes include $\text{HPO}_4^{2-}$, and $\text{CO}_3^{2-}$. $Z$ is usually $\text{OH}^-$, $\text{F}^-$, $\text{Cl}^-$, or $\text{Br}^-(7)$. Apatite is an ideal material for long-term containment of contaminants because of its low water solubility ($K_{\text{sp}}>10^{-40}$), high stability under reducing and oxidizing conditions and over a wide temperature range, availability, and low cost (8,9). It is well documented that calcium apatite strongly sorbs uranium (10-13), strontium (14-17), lead (18-21), selenium (22), and nickel (23). Apatite can be isolated from animal bone (24,25) or synthesized by precipitation from aqueous solutions (26) or by solid state reactions at high temperature (27).

For uranium, Jeanjean et al. (28) reported uranium strongly sorbs to hydroxyapatite in batch experiments. The authors report the uranium forms a microcrystalline phase through dissolution - precipitation mechanism. Arey et al. (29) performed batch experiments with uranium and synthetic hydroxyapatite. In the experiments apatite reduced uranium concentration in water to below the solubility of autunite $[\text{Ca (UO}_2\text{)}_2(\text{PO}_4\text{)}_2\cdot\text{H}_2\text{O}]$, a uranyl phosphate mineral thought to control the concentration of uranium in phosphate rich systems. The authors concluded uranium concentrations in the presence of apatite appear to be controlled by the precipitation of secondary phosphate phases, however the authors did not identify these phases. Ordonez-Regil et al. (13) studied the sorption of uranium onto natural fluorapatite. Starting with a uranium solution of $1 \times 10^{-4}$ M, The authors report 90% of the uranium was sorbed to the fluorapatite in 45 minutes. XRD analysis indicated the growth of uranyl species into the fluorapatite. Results from work performed in Sandia National Laboratories with apatite derived from cow bone further demonstrate the ability of apatite to sorb uranium. In batch experiments with initial uranium concentrations of $1 \times 10^{-5}$ to $1 \times 10^{-7}$ M and using 25 mL of solution with 0.1 to 0.01 g of apatite, $K_d$ values for uranium sorbed to apatite were determine to range from 100 to 520 mL/g. In desorption experiments less that 1% of the sorbed uranium was desorbed even under oxidizing conditions created by adding hydrogen peroxide to the liquid phase.

The hypothesis for the use of natural apatites to remove dissolved uranium from groundwater is that they provide a source of phosphate with which aqueous U(VI) should react to form insoluble uranyl phosphates, such as hydrogen, calcium, magnesium, potassium or sodium autunite $[\text{Ca(UO}_2\text{)}_2(\text{PO}_4\text{)}_2\cdot10\text{H}_2\text{O}]$ (6,30,31). The effectiveness of removal of aqueous uranium by commercially available natural apatite materials (phosphate rock, bone meal, and bone meal charcoal) was determined in laboratory batch sorption and column experiments. The results of the laboratory evaluation were used for choosing specific phosphate material for the field demonstration. Other criteria for choice of material for use in PRBs include the extent of reversibility of uranium removal, permeability of the reactive material, and potential release of solutes detrimental to water quality.

The removal of dissolved uranium in water by hydroxyapatite is postulated to occur by the formation of a uranyl phosphate phase, in part because of the low solubilities of uranyl phosphates such as various forms of autunite (Ca, Mg, Na, or H uranyl phosphate). However, because there are many uranyl phosphate phases and the solubility constants for some of these phases are not well defined, extended X-ray absorption fine-structure spectroscopy (EXAFS) was used (32) to characterize the process of uranium uptake by apatite on a molecular scale since calculation of the degree of saturation for these phases cannot be used to determine the precipitation of a specific phase. Instead, spectroscopic and X-ray diffraction techniques were used to characterize the process of uranium uptake. In addition, it is unclear whether uranium removal occurs by precipitation directly from solution or by reaction at the apatite surface. Knowledge of the process of uranium uptake by phosphate materials is needed for modeling uranium transport in the PRB. The U-edge EXAFS spectra are characteristic of the local bonding environment of uranium. The spectra are used for phase identification by comparing with spectra.
of phases of known structure. In addition, the distance and coordination number of the nearest and next-nearest neighboring atoms to uranium can be derived from sample spectra for comparison to distance and coordination of likely bonding environments. Synchrotron-source X-ray diffraction (XRD) also was used to identify the presence of crystalline uranyl phase in the reacted apatite materials. This technique provides significant greater angular resolution and sensitivity than standard laboratory XRD instruments (33).

Synchrotron-source XRD patterns of these samples also did not indicate presence of any known uranyl phosphate phase. Crystalline U(VI)-phosphate solids, autunite and chernikovite \[\text{(H}_3\text{O})_2\text{(UO}_2\text{)(PO}_4\text{)}_2\cdot6\text{H}_2\text{O}\] were present only in XRD patterns of reagent grade hydroxyapatite with uranium uptake concentration of greater than 7,000 ppm. Detection limits of about 350 ppm and 2,000 ppm uranium, were determined for autunite and chernikovite, respectively. No evidence for these crystalline precipitates were observed in any of the samples prepared from bone-char materials, which had U(VI) solid concentrations ranging from 800 to 5,500 ppm. These results, in combination with EXAFS measurements, suggest that the predominant U(VI) removal process is complexation by phosphate in the apatite surface (e.g. adsorption) at uptake levels of column experiments or expected in the field demonstration (33).

4.2. Mechanism of Uranium Removal from Ground Water Using Zero Valent Iron (Fe°)

A concerted effort is under way to remediate ground water contaminated with radionuclides (e.g. \(^{99}\)Tc, U), other regulated metals (e.g., Hg\(^{2+}\), Cr\(^{6+}\)), and volatile organic compounds (VOCs) using zero-valent iron (ZVI, Fe\(^0\)). Zero-valent iron has been identified as a leading potential technology for use in remediation effort. Previous works have demonstrated that ZVI can effectively remove Cr\(^{6+}\), Hg\(^{2+}\), Ag\(^{1+}\), Tc\(^{7+}\), and U\(^{6+}\) from solution (34).

Soluble uranium (UO\(_2\)\(^{2+}\)) is associated with both toxicity and cancer risks for the potential human receptors surrounding contaminated areas. Studies have shown that iron based minerals, such as pyrite or magnetite, can effectively adsorb uranium from ground water under favorable conditions (i.e., \(E_h\), pH, dissolved O\(_2\), etc.). Recently Cantrell et al. (35) were able to show that ZVI particles can be used to rapidly remove UO\(_2\)\(^{2+}\) from a surrogate ground water stream. They proposed that U\(^{6+}\) may be removed from solution by any of three mechanisms: (a) reduction of U\(^{6+}\) by ZVI to form the less soluble U\(^{4+}\) (i.e., UO\(_2\).xH\(_2\)O) phase, (b) sorption onto iron oxide corrosion products by ion exchange with hydroxyl sites, or (c) a combination of reduction/precipitation.

Sorption, as a removal mechanism, is not preferred because soluble uranium will remain in its more soluble oxidation state, thereby lending itself to be easily transported by the colloidal iron corrosion products. Due to the reversible nature of the sorption mechanism, another concern is the potential release of soluble uranium back into the ground water. Reduction of U\(^{6+}\) to U\(^{4+}\) is the preferred removal mechanism since the resulting U\(^{4+}\) species is less soluble and thus less mobile in ground water, assuming that the U\(^{4+}\) species is not colloidal. Therefore, the solubility of uranium in ground water plays an important role when considering effective strategies for its remediation (36).

Thermodynamically, reduction from U(VI) to U(IV) is favorable in strong acidic media as indicated by the modest positive value for the standard cell potential, \(E^0\) in eq 1 (36):

\[
\text{Fe}^0 + 1.5\text{UO}_2^{2+} + 6\text{H}^+ = \text{Fe}^{3+} + 1.5\text{U}^{4+} + 3\text{H}_2\text{O}
\]

\[E^0 = +0.17 \text{ V} \quad (1)\]

However, Wersin et al. (37) reports that reduction of U(VI) to the less soluble U(IV) oxidation state is relatively slow under acidic conditions. Similarly, reduction of U(VI) by (Fe\(^{2+}\)) has been reported by Baes to be kinetically slow (38). It has been speculated that uranium contaminants
are removed by ZVI via a heterogeneous surface reaction (e.g., reduction, adsorption, and/or coprecipitation) that is able to render the uranium contaminants insoluble and thus immobilize them onto the ZVI or iron oxide surface. It has also been long understood that the oxidation state of uranium is one of the determining factors that governs its solubility, speciation, and sorptive behavior (37).

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique whose strength lies in its ability to determine the various chemical states of a given surface species. Bancroft et.al (1990) and Dillard et.al (1988) reported that XPS can be a valuable spectroscopic tool when studying the metal sorption processes, such as redox reactions, on oxide, clay, and sulfide systems (39,40). Other analytical methods, such as wet chemistry, used to determine the quantitative speciation of uranium often underestimate the contribution from $U^{4+}$ due to reoxidation (41). Therefore, XPS offers an advantage over wet chemistry methods and provides a more accurate technique for monitoring the oxidation state of uranium on iron surfaces. Using experimental design, it will be able to monitor the uranium speciation in a synthetic surrogate of Bear Creek Valley ground water. This can be done using ZVI under the two limiting conditions of aerobic (oxi) and anaerobic (anoxic) experienced in remediation schemes using ZVI. By carrying out the experiments at constant pH (i.e., ~6.0), the uranium speciation will be kept relatively constant (42-44). The experiments will provide boundary conditions in that the aerobic experiment will thermodynamically favor the sorption mechanism of uranium to the Fe$^{3+}$ corrosion products, while the anaerobic experiment will favor the reduction of $U^{6+}$ to $U^{4+}$. Redox potential, pH measurements, $\gamma$-counting of the solution will be performed to assist in determining the most thermodynamically stable uranium species and the most kinetically favored mechanism of interaction of ZVI with uranium under the varying conditions of dissolved oxygen concentration (36).

Some of the more important reactions that may occur during treatment of metals (e.g., inorganics) with ZVI include the following processes:

**anaerobic corrosion**

$$2H_2O + Fe^0 = Fe^{2+} + H_2 + 2OH^- \quad (2)$$

**aerobic corrosion**

$$O_2 + 2Fe^0 + 2H_2O = 2Fe^{2+} + 4OH^- \quad (3)$$

$$Fe^{3+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O = Fe(OH)_3(s) + 2H^+ \quad (4)$$

**cementation**

$$M^{n+} + Fe^0 = M^{n+2} + Fe^{2+} \quad (5)$$

**sorption / ion exchange**

$$>OH + M^{n+} = >OM^{n+1} + H^+ \quad (6)$$

For the aerobic experiment, equations 3, 4, and 6 represent the most likely reaction mechanism. The ZVI coupon is first oxidized in solution to form a ferrous iron ($Fe^{2+}$) layer. In turn, the ferrous iron is rapidly oxidized (eq 4) to form a high surface area and highly porous layer of hydrolyzed ferric ($Fe^{3+}$) oxide. Hydrolyzed ferric iron [Fe(OH)$_3$(s)] and its polymer, ferrihydrate, are effective in removing $U^{6+}$ by sorption (eq 6) (45-49). In eq 6, the $>OH$ represent an exchangeable site on the hydrous metal oxide at the hydrous iron substrate or on its detached corrosion product. In the simplified eq 6, depending on the solution pH, the surface site may have a net positive charge ($>OH_2^+$) or negative ($>O^-$) charge. The exchange of protons to and from the oxide surface creates specific site types available for adsorption. For most iron-containing minerals, the solution pH value that results in no net charge on the mineral (i.e., the point of zero charge pzc) is typically in the range of approximately 6-8 (50). As the solution pH falls below the pzc of the substrate, the net surface charge becomes more positive, favoring the sorption of anionic species; conversely, as the pH is increased above the pzc, the substrate becomes more negatively charged, favoring the sorption of cationic species. If the iron surface contains roughly equal amounts of positive and negative charges at pH 6.0, which is close to pzc...
of the iron substrate, sorption of U(VI) by the iron surface can take place with the negatively charged \( \text{UO}_2(\text{CO}_3)_2^{2-} \) species as is suggested by Payne and Waite (42).

For the anaerobic investigations, the “cementation” reaction seen in eq 5 \((M = \text{uranium or } \text{UO}_2^{2+})\) most readily describes the mechanistic pathway by which soluble U\(^{6+}\) is removed from solution. Under strongly reducing anaerobic conditions and given enough time, ZVI can partially reduce U\(^{6+}\) to U\(^{4+}\), which is consistent with the literature for reduction of U\(^{6+}\) by Fe\(^{3+}\) or H\(_2\) in that reduction of U\(^{6+}\) appears to be kinetically slow. Therefore, the relative significance of soluble uranium removal by reduction using ZVI under treatment trench conditions is uncertain. Perhaps, with a deep enough treatment zone to provide the necessary anaerobic conditions and the required contact time, this mechanism could represent a significant component to the overall removal of soluble uranium, if any remains after the semi-oxic contact zone, which offers a relatively rapid removal of U\(^{6+}\) by sorption to corrosion product. Thus, if the residence time in a treatment trench is relatively short (e.g., less than a few hours) and anoxic conditions are not achieved fairly rapidly, then kinetically slow reduction of U\(^{6+}\) is not likely to be significant component of the overall removal. In the middle of a treatment trench, where anoxic conditions begin to prevail, the pH values will be considerably higher than pH 6 due to the production of hydroxyl ions from the relatively slow anaerobic corrosion of the iron substrate (eq 2). This is detrimental to the reduction mechanism because higher pH values (>8) tend to disfavor reduction of U\(^{6+}\) and favor sorption. Therefore, under practical groundwater remediation conditions, sorption appears to have more significant role than reduction in the removal U\(^{6+}\) using ZVI. Most of the soluble uranium removal occurs under semi-oxic conditions near the forward portion of the column or trench, where U\(^{6+}\) can bind avidly to the corrosion product containing Fe\(^{3+}\). Thus, there will be little additional uranium removal downstream by reduction due to (a) unfavorable kinetics in the near-neutral to alkaline solution and (b) a low concentration of residual soluble U\(^{6+}\) available to be reduced (36).

In conclusion, iron coupons tested under controlled conditions indicate that under fully aerobic conditions sorption of U\(^{6+}\) to hydrated Fe\(^{3+}\) corrosion products is the predominant removal mechanism. The strong affinity for uranium by iron-containing minerals is well documented (45-49). However, a potential concern with this removal mechanism is the possible redispersion and/or desorption of U\(^{6+}\) on detached fine particulate corrosion products. Although, treatment by ZVI of subsurface water, with low levels of dissolved oxygen, should minimize this effect. When reaction conditions (pH and U speciation) are similar but with the exclusion of dissolved oxygen, soluble uranium is slowly removed at the iron surface by partial reduction of U\(^{6+}\) to sparingly soluble U\(^{4+}\) species. Uranium speciation was verified using XPS. These results are similar to those reported by Grambow et al (41).

### 4.3. Use of Magnesium Oxide at the Waste Isolation Pilot Plant

At the Waste Isolation Pilot Plant (WIPP), located in Carlsbad, New Mexico, magnesium oxide was chosen as the backfill material to aid in preventing migration of radionuclides from the repository. The WIPP is located in a salt dome approximately 2000 feet below the surface. It is suspected that any liquid that comes in contact with the waste will be brine composed mainly of sodium chloride. The WIPP is designated for transuranic waste only. The waste is mainly composed of radionuclide contaminated clothing, tools, and other materials used in the processing of radionuclides, solidified liquid and sludge wastes, and old glove boxes.

Magnesium oxides perform several functions to prevent radionuclide migration. First, in contact with a WIPP brine, magnesium oxide reacts with water to form magnesium hydroxide. Magnesium hydroxide in water maintains the solution pH between 8.5 and 9.5 in WIPP brines. At this pH actinides have their lowest solubility in WIPP brines. Second, magnesium oxide provides magnesium to complex with organic chelators in the repository. Organic chelators including
oxalic acid, EDTA, citric acid, and acetic acid were used in processing or in decontamination and are contained in the waste to be placed in the WIPP. These organic chelators will complex with the actinides and increase their solubility. Additionally the organic chelators increase the mobility of actinides because the organic-actinide complexes have lower sorption properties to soils than the actinides alone. The magnesium provided by the magnesium oxide backfill competes with the actinides for complexation with the organic chelators. The third function of the magnesium oxide backfill is to prevent buildup of carbonate in brines that may contact the waste in the repository. Carbonate complexes with actinides and increases actinide solubility. The magnesium hydroxide formed by the reaction of magnesium oxide with the WIPP brine reacts with carbonate to form insoluble magnesium carbonates and prevent actinide carbonates from forming at high concentrations (51).

5. Site Characterization and Design Parameters

When assessing site conditions to determine the feasibility of using a PRB, four general subsurface properties must be measured: plume characteristics, hydrogeology, geochemistry, and microbial activity. Typically, wells are installed for sampling. But push technologies, which are quicker and cheaper, are becoming available. They can be used to assess several depths along a vertical axis in order for the plume to be more fully characterized (1).

5.1. Plume Characteristics

Concentrations and spatial distributions of contaminants must be fully characterized so that the barrier (hydroxyapatite, ZVI, magnesium oxide) can be positioned to treat the entire plume. Predictions must be made about the plume’s future movement. Knowledge of vertical distribution is essential so that the contamination cannot flow over or under the reactive area or so that money is not lost by making the barrier too large. The barrier is installed down-gradient from the plume’s center of mass (1). It must be determined whether the center of mass is moving and if it will reach the barrier. The behavior of the plume’s constituents must be characterized. As some transformation products are toxic, the barrier must be designed to treat these compounds. Therefore, an understanding of not only what contaminants are in the plume, but also of their chemical properties is essential for properly determining the necessary residence time (52). When radionuclides are present, radiation is of concern. Therefore, isotopic analysis and gross alpha and beta counts are needed for a thorough plume characterization (53).

5.2. Hydrogeology

Because the system is passive, all of the contamination must reach the barrier by natural groundwater flow. Therefore, hydraulic determination is the most important part of site characterization (54). Porosity, conductivity, and the effects of any pumping near the site must be taken into account. Barriers are usually placed at least two feet above the water table to account for these fluctuations (55). Depth to bedrock and the presence of any large impermeable rocks will affect barrier placement. Often the barrier must be keyed at least one foot (55) into the bedrock to prevent underflow. Any fractures in the impermeable layer must be identified and sealed so that contaminants cannot escape (1). Alternatively, a geotextile fabric or concrete layer can be applied horizontally under the PRB to prevent underflow (55). The hydraulic gradient, which is the change in hydraulic head over a distance, can be determined in all three dimensions. Vertical determinations of the gradient indicate whether underflow could pose a problem.
5.3. Geochemistry

To maximize a barrier’s performance and foresee any possible troubles, geochemical measurements must be taken. These include pH, dissolved O₂, E₈H, carbonate alkalinity, and concentrations of species that can react in the conditions created by the media. These can include SO₄²⁻, Ca, Fe, Mg, Al, Ba, Cl, F, CO₃²⁻ (and protonated species) (1). Many of these species are important because they can affect precipitation formation, which can decrease reactivity by coating available surfaces and can lower permeability by clogging pore spaces. For example, calcite (CaCO₃) or siderite (FeCO₃) buildup can occur if concentration of Ca, dissolved Fe, or CO₃²⁻ are high. The pH can affect the amount of CO₃²⁻ available for solid formation because it exhibits acid-base behavior. Dissolved O₂ can cause ferric hydroxide precipitation formation. If the area is anoxic, then ferrous hydroxides will dominate, which do not cause clogging problems (1). Precipitate buildup is of importance because it can decrease permeability. This forces groundwater to flow through a smaller pore volume, which increases velocity and lowers residence time. This could result in contaminant break-through (54). Conductance, salinity, and turbidity measurements are also important (53). Turbidity can be an indication of colloids or microbial communities. Colloids can be problematic if contaminants sorb to them and are carried down-gradient of the barrier.

5.4. Microbial Activity

Microbial communities can participate in complex interaction in the reactive zone. Many aspects of their role in remediation with PRBs have not yet been elucidated. They can be detrimental to the barrier’s performance if their overgrowth causes plugging. Phospholipid fatty acid analyses can be performed to determine the reactive area’s potential for biofouling roles. SRBs reduce SO₄²⁻ to S²⁻ so that insoluble metal sulfides can be formed (1). This is a significant removal mechanism for contaminant metal cations.

6. Radioactive Waste Classification

6.1. Radioactive Waste Definition

According to the IAEA, (56) “radioactive waste may be defined as material that contains, or is contaminated with, radionuclides at concentrations or activities greater than clearance levels as established by the regulatory body in each country, and for which no use is foreseen”. In this definition, there are several important concepts to consider. First, it should be recognized that this definition is used primarily for legal and regulatory purposes because material with activity concentrations equal to or less than clearance levels is still radioactive from a physical point of view (although the associated radiological hazards are considered negligible). Second, clearance levels are defined and established by the individual Member State and its regulatory body. Therefore, these levels, and the ensuing radioactive waste classification system, may differ slightly from country to country.
6.2. IAEA Radioactive Waste Classification

According to the IAEA radioactive waste classification (57), the principal waste classes include low and intermediate level waste, which may be subdivided into short lived and long lived waste, and high level waste. The waste released from nuclear regulatory control, in accordance with clearance levels, is called “exempt” or, more preferably, “cleared” waste.


According to the U.S. Radioactive Waste Classification, radioactive waste is classified into six categories (58):

- Spent nuclear fuel from nuclear reactor
- High level radioactive waste from the reprocessing of spent fuel.
- Transuranic radioactive waste (TRU), resulting mainly from manufacture of nuclear weapons.
- Uranium mill tailings from the mining and milling of uranium ore.
- Low level radioactive waste, generally in the form of radioactively contaminated industrial or research waste.
- Naturally occurring and accelerator produced radioactive materials (NARM)

7. Radioactive Waste in Egypt

It is well known that, Egypt has a variety of radiological sources. Although a nuclear power reactor has not yet been built, there are two research reactors used for the production of isotopes for industrial and medical applications and research on neutron physics and personnel training. One of the research reactors is an operation 2 MW water moderate reactor, the other is a 22 MW open pool multipurpose reactor MPR. Moreover, radioactive sealed sources are used throughout the country for medical diagnosis and treatment as well as in industrial application, such as gamma radiography. In addition, Co-60 sterilization facility (`370,000 Ci) operates at the National Center for Radiation Research and Technology in Cairo. Some of these sealed sources are still in service, while others are no longer in use or are unwanted. Widespread use of radioisotopes in different applications effects the generation of applicable amount of radioactive waste (59).

7.1. Common sources of radioactive waste in Egypt

- Research activities: Research activities include a variety of activities and facilities such as research reactors, accelerators, and laboratory activities. All may generate radioactive waste, with the type and volume of the waste department on the research conducted.
- Radioisotope production: The type and volume of radioactive waste produced depends on the radioisotope and its production method. Generally, the volume of radioactive waste generated from these activities is small but specific activities might be significant.
- Radioisotope application: The use of radioisotopes in medical (like technetium generator) and industrial applications may generate small volumes of radioactive waste. The type and volume of radioactive waste produced will depend on the application.
• Unwanted or disused radioactive sealed sources: These sources were used in different radioisotope applications and now no longer in use and no further use is foreseen. These types of sources should be considered as a spent radioactive sources
• Spent reactor fuel.

7.2. Radiochemical Composition of LLW

According to El-Sourougy (59), the composition of LLW in Egypt is as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Quantity (Ci/l)</th>
<th>Element</th>
<th>Quantity (Ci/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caesium-137</td>
<td>4E+7</td>
<td>Iodine-131</td>
<td>5E+9</td>
</tr>
<tr>
<td>Strontium-90</td>
<td>6E-8</td>
<td>Zirconium-95</td>
<td>3E-9</td>
</tr>
<tr>
<td>+ Yttrium-90</td>
<td></td>
<td>+ Niobium-95</td>
<td></td>
</tr>
<tr>
<td>Ruthenium-106</td>
<td>5E-8</td>
<td>Cerium-144</td>
<td>2E-8</td>
</tr>
<tr>
<td>+ Rhodium-106</td>
<td></td>
<td>+ Praseodymium-144</td>
<td></td>
</tr>
<tr>
<td>α- Emittner</td>
<td>1E-8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.3. Sealed Radioactive Sources in Egypt

Sealed radioactive sources (SRS) have been widely used over the world for many decades in industry, medicine, and research. The definition of SRS, according to the International Basic Safety Standards for Protection Against Ionizing Radiation and for Safety of Radiation Sources (60) is, “a radioactive material that [is] either permanently sealed in a capsule or closely bounded and in a solid form.” The activity of such sources varies from a few kilobecquerel in consumer products to petabecquerel for irradiation, sterilization and radiotherapy. According to the IAEA information (61), a large number of SRS exist through the world, both in developed and developing countries. This number is believed to be in the order of millions. SRS needs to be kept under regulatory control during their entire lifetime until they are safely disposed of or have decayed to accepted clearance levels. Development of some engineering barriers that can be use in conditioning of such sources is very important to decrease the risk and hazard of radionuclides resulting from its migration.

Table (2) lists the inventory of spent sources in Egypt, according to the IAEA, (62) as well as its applications in medicine, industry and research fields according to Van Blerk et al. (63).
Table (2): The inventory of spent sources in Egypt according to the IAEA (62) as well as its applications in medicine, industry and research fields according to Van Blerk et al. (63).

<table>
<thead>
<tr>
<th>Source Type</th>
<th>Number</th>
<th>Total Activity (Ci)</th>
<th>Source Activities</th>
<th>Applications</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>266</td>
<td>$2.22E+1$</td>
<td>50-500 MBq</td>
<td>Manual Brachytherapy</td>
<td>Small portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 10 GBq</td>
<td>Remote brachytherapy</td>
<td>Mobile units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50-1000 TBq</td>
<td>Teletherapy</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50-1000 TBq</td>
<td>Whole blood irradiation</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Up to 750 TBq</td>
<td>Research</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Up to 220 TBq</td>
<td>Gamma Radiosurgery</td>
<td>Skull caps</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;1$-1 TBq</td>
<td>Industrial radiography</td>
<td>Portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$0.2$-20 GBq</td>
<td>Level gauge</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;1$-400 GBq</td>
<td>Sterilization</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-100 TBq</td>
<td>Calibration facilities</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-100 TBq</td>
<td>Dredgers</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 GBq</td>
<td>Brain tumor control</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;1$-1000 TBq</td>
<td>Irradiators</td>
<td>Fixed installations</td>
</tr>
<tr>
<td>$^{57}$Co</td>
<td>-</td>
<td>-</td>
<td>Up to 400 MBq</td>
<td>Calibration sources</td>
<td>Fixed or mobile units</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>44</td>
<td>$3.17E+1$</td>
<td>50-1500 MBq</td>
<td>Manual Brachytherapy</td>
<td>Small portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03-10 MBq</td>
<td>Remote brachytherapy</td>
<td>Mobile units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01-2 MBq</td>
<td>Teletherapy</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1-400 GBq</td>
<td>Whole blood irradiation</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Up to 13 TBq</td>
<td>Research</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;0.4$ MBq</td>
<td>Calibration sources</td>
<td>Fixed or mobile units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-100 GBq</td>
<td>Well Logging</td>
<td>Portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$0.1$-2 GBq</td>
<td>Moisture detector</td>
<td>Portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$0.14$-40 GBq</td>
<td>Conveyor gauge</td>
<td>Fixed installation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-20 GBq</td>
<td>Density gauge</td>
<td>Fixed installation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$0.1$-20 GBq</td>
<td>Level gauge</td>
<td>Fixed installation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$0.1$-400 PBq</td>
<td>Sterilization</td>
<td>Fixed installation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-100 TBq</td>
<td>Dredgers</td>
<td>Fixed installation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;1$-100 TBq</td>
<td>Calibration facilities</td>
<td>Fixed installation</td>
</tr>
<tr>
<td>$^{241}$Am/Be</td>
<td>40</td>
<td>$3.05E+2$</td>
<td>1-800 TBq</td>
<td>Well logging</td>
<td>Portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1-2 MBq</td>
<td>Moisture detector</td>
<td>Portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-10 GBq</td>
<td>Bone densitometry</td>
<td>Mobile units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;1.4$ MBq</td>
<td>Density gauge</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50-500 MBq</td>
<td>Static eliminators</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5-5 MBq</td>
<td>Lightning preventer</td>
<td>Fixed installations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.02-3 MBq</td>
<td>Smoke detectors</td>
<td>Fixed units</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>124</td>
<td>536 (mg)</td>
<td>30-500 MBq</td>
<td>Manual Brachytherapy</td>
<td>Small portable units</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;10$ MBq</td>
<td>Calibration sources</td>
<td>Fixed installation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200-1300 MBq</td>
<td>Manual Brachytherapy</td>
<td>Small portable sources</td>
</tr>
<tr>
<td>$^{192}$Ir</td>
<td>-</td>
<td>-</td>
<td>0.1-1 TBq</td>
<td>Vascular Brachytherapy</td>
<td>Catheterization</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1-5 TBq</td>
<td>Industrial radiography</td>
<td>Portable units</td>
</tr>
<tr>
<td></td>
<td>238Pu</td>
<td>226Ra/Be</td>
<td>241Am-Be</td>
<td>226Ra/Be-137Cs</td>
<td>169Yb</td>
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</tbody>
</table>

7.4. Choosing Suitable Backfill Material for Inshas Site

When activity levels increase, there is also a corresponding increase in the need to isolate the waste from the biosphere. In the biosphere suitable disposal options range from simple and conventional methods to highly engineered geologic isolation. In addition, when activity levels increase, there is also an increased need to consider shielding from radiation, and the generation of heat from radioactive decay.

Suitable, radioactive waste may be:

- Stored for decay and then exempted like short lived radionuclide unsealed or sealed (unwanted sealed sources),
- Disposed of in near surface facilities (as a new site in Inshas now), or
- Isolated from the biosphere in deep geological formations for long-lived radionuclides both unsealed and sealed (unwanted sealed sources).

In this case, backfill materials play an important part in prevention of the migration of radionuclides towards the ground water. The factor of disposal time may reach to hundreds of years.

7.4.1. Inshas Site Characterization

7.4.1.1. Geomorphology

Many studies have dealt with the geological situation of the Inshas area and it’s surroundings; (64,65), (66), (67,68). The final results of these previous studies show the Inshas area is characterized by low relief topography. The surface rarely exceeds 100 m above the sea level. The area is distinguished into three main physiographic features: (68), marginal plain part, foot-hill part and table land part.
7.4.1.2. Stratigraphy (Surface and Subsurface Geology)

According to said (69), the region is essentially occupied by tertiary to quaternary rocks with mid-tertiary basalt flows. This succession composes typically shallow marine and continental environment as well as deltaic deposits. According to Attia studies (70), the subsurface section includes three stratigraphic units:

- **Quaternary deposits**: constituted of variable proportions of sand, clays, and gravels, occasionally covered by thin layer of wind blown sand. The thickness of this sediments ranges between 10 and 40 m inside the area belongs to the Inshas nuclear research center and reaches 62 m in the vicinity of El-Insha drillhole (65).
- **Miocene deposits**: exposure of Miocene sediment cropout on the surface, three km to the east of Ismailia canal at Inshas site. They consist mainly of greenish clay and limestone (65).
- **Mid-Tertiary basalt**: basalts in form of sheets are common in the area, although they are exposed only at Abu Zaabal quarry. The depth to basalt is not uniform in this area (65).

7.4.1.3. Meteorology

According to Tawfic and Abdel All studies (71,72), Egypt lies within the Northern African Desert Belt. Its general climatic characteristics are, therefore, low annual rainfall and considerable seasonal and daily temperature range. The main meteorological events related to Inshas area from 1982 to 1991 are:

- Average air temperature: 21.5°C
- Extreme air temperature: 6.1-41.4°C
- Average humidity: 61.3%
- Average annual precipitation of rainfall: 20.8 mm
- Maximum annual precipitation of rainfall: 28.1 mm
- Mean value of sandstorms: 0.8 days per year
- Maximum value of sandstorms: 3.0 days per year
- Mean value of evaporation: 2.2 HP
- Maximum value of evaporation: 2.3 HP

7.4.1.4. Hydrological Analysis

The main source of groundwater in Inshas site and it’s surroundings is the seepage from the Ismailia canal. Rainfall on the southern portion of the area, although scarce, eventually feeds into the water bearing formation in the area. The catchment area collects rainwater in some stormy seasons (73). In general, ground water flow is in the eastward direction or precisely to the northeast direction. This trend holds true in the western portion of the Ismailia canal. The absolute level of the groundwater is usually 13 to 13.5 m above the sea level, which coincides with the level of the surface water at the Ismailia canal. This fact together with the fact that the surficial sediments are of Nilotic origin indicate the groundwater at Inshas site is connected with the Nile water (65). The direction of the flow of groundwater is expected to be perpendicular to the canal line. The canal could be feeding the groundwater most of the time.
7.4.1.5. Hydrochemical Analysis

According to Hem, (74) classification of groundwater, and analysis of the groundwater at Inshas site, from the quaternary aquifer shows that it is related to the fresh water category (0-1000 mg/l total dissolved solids).

8. Waste Management Programs in Different Countries

8.1. Waste Management in Finland

Nuclear power plants produce about 30% of the electricity in Finland. According to Posiva, (75) the Finnish Nuclear Waste Program consists of handling and management of low and intermediate level waste, the final disposal of the spent fuel and operating waste, as well as decommissioning of nuclear power plants. There are four nuclear power plants operating in Finland: the BWRs (2 X 710 MW) at Olkiluoto operated by TVO, and the PWRs (2 X 445 MW) at Hastholmen operated by IVO. Until 1996, TVO and IVO had the responsibility of management of the spent fuel. In January 1996, a new company, Posiva, took over the responsibility of management the spent fuel in Finland. Progress of the waste management program is controlled and supervised by regulatory bodies. In Finland, the Ministry of Trade and Industry is responsible for licensing of nuclear waste facilities while, the Finnish Center for Radiation and Nuclear Safety (STUK) is responsible for supervision of safety. Arrangements for the disposal of low and intermediate level waste were started in the 1980s. After geological investigations, two repositories have been constructed; one of them at Olkiluoto and the other at Loviisa. Arrangements for the final disposal of spent nuclear fuel have been made in Finland since the early 1980s. For that purpose, a siting process was begun in 1983 with a country-wide survey of the principal geological features in Finland. According to TVO, (76), the results of the studies carried out indicate that Finnish bedrock is suitable for building a safe repository. Construction of the final disposal facility should start during the 2010s and operation should begin around 2020.

8.2. Management of Spent Nuclear Fuel in Taiwan

In Taiwan, there are three, twin unit, nuclear power plants in operation with a total output of 5145 MW. The spent nuclear fuel resulting from these nuclear power plants may cause a severe environmental impact unless it is disposed of in a suitable disposal facility. For this purpose, Taiwan Power Company (TPC), the only nuclear power plant operator in Taiwan, has conducted a long-term disposal program for the spent nuclear fuel. TPC has three programs to achieve a final disposal site. In Phase I of the program (1986-1988), TPC contracted the Institute of Nuclear Energy Research (INER), the Energy and Resources Laboratories (ERL) and the Center Geological Survey (CGS). The main purpose of this phase was to study the siting criteria, siting investigations and design concept on the final disposal site. In Phase II of the program (1988-1991), TPC again contracted the INER, ERL, CGS, and the National Tsing-Hwa University. The tasks of this phase were to plan a long-term program for the spent nuclear fuel disposal and to perform a preliminary geological investigation for screening the potential disposal site. Phase III of the program (1991-2031) is a long-term phase, proposed as a guideline for the development of Taiwan’s spent nuclear fuel disposal program (77).
8.3. Management of Radioactive Waste from the Operation of Nuclear Power Plants

In Germany, there are 19 nuclear power plants in operation with a total energy of about 21,700 MW. These nuclear power plants produce about 6500 m$^3$ of solid wastes and 1500 m$^3$ of liquid wastes. GNS, a German company (1977), is responsible for the management of waste resulting from the nuclear power plants in Germany. The wastes managed by GNS can be divided into two categories; waste from operations and decommissioning, and waste from the nuclear fuel cycle (spent nuclear fuel). The main strategies of nuclear waste management are: transform the waste into physically and chemically stable products suitable for interim storage and final disposal, and reduction of the waste volume for interim storage and final disposal. Reduction of the solid waste volume is achieved by using a high-pressure compactor. The final compacted wastes are packaged in final disposal containers, 200-1-drums. Reduction of solid waste volume takes place by incineration and the residues are also compacted in the high-pressure compactor. Rubble and thick-walled metallic parts considered stable enough for final disposal can hardly be reduced in volume. Activated core components are cut in the storage pools in the power plants, under water, using remote control, and are packaged in thick-walled cast iron casks. Liquid wastes (evaporator concentrates, waste water from decontamination) and moist wastes from the purification of water (resins) are dried or dewatered, with the aid of various processes, to bring into a form suitable for interim storage and final disposal. In Germany, there are two strategies for management of the spent nuclear fuel: reprocessing abroad with the return of the wastes generated in the process (predominant), or direct final disposal. For direct final disposal of the spent nuclear fuel, the fuel can be stored for the interim in CASTOR casks at two sites operated by GNS, at Gorleben (1995) and Ahaus (1992) with a total capacity for each of 400 places for casks. Wastes generated from reprocessing of spent fuel abroad, which is return back, are stored in large casks in Gorleben, similar to spent fuel, before they can be brought to a final repository (78).

8.4. Waste Management Optimization at COGEMEA

Spent nuclear fuel is produced as a result of nuclear power plants. The different steps of the nuclear fuel cycle are the extraction of uranium compounds, enrichment of purified uranium, fabrication of assemblies, reprocessing and waste conditioning, and finally recycling. When the spent fuel assembly leaves a reactor, the ashes of combustion consisting of fission products represent only 3% of the spent fuel, while uranium and plutonium contents are 96% and 1%, respectively. The uranium is still enriched with a fissile $^{235}$U grade between 0.8 and 0.9%, while the plutonium’s fissile isotopes are about 70% of the whole quantity. COGEMEA, an international waste management center, has developed an optimization policy of reprocessing and recycling valuable materials to decrease waste volume and waste radiotoxicity before disposal in sub-surface as well as deep repositories. At COGEMEA, reprocessing the spent fuel as a preliminary treatment to separate uranium and plutonium from the ultimate residues closes the fuel cycle. The recoverable energy from plutonium through recycling in the current light water reactors (LWRs) is at least 1-2 ton oil equivalent g$^{-1}$. The residues are conditioned in stable qualified packages until recovering such a quantity of energy. Uranium and plutonium are re-used to produce mixed oxide (MOX) fuel assemblies, which will be burned in a reactor. Reprocessing of the spent fuel decreases the final volume of waste disposed in the geological repositories as well as decreases the radiotoxicity by recycling plutonium back into the energy system (79).
8.5. The U.S. DOE Strategy For Permanent Disposal of Commercial LWR, Spent Nuclear Fuel

In the U.S. processing of spent commercial reactor fuel has not been performed since the 1970s. This is due to proliferation problems resulting from separation of plutonium. Because of that reason, the U.S. decided to perform the one-through nuclear fuel cycle with direct disposal of unprocessed, zircaloy-clad LWR spent fuel rods within metal canisters in a geologic repository. Yucca Mountain, Nevada, is the only potential repository site that is being evaluated in the U.S. The present disposal strategy may prove to be unacceptable due to two reasons. The first reason, (81-83) comes from the U.S. policy, which confirms that reactor-grade Pu in LWR spent fuel can be used effectively for nuclear weapons. As a result of this policy, it may pose unacceptable risk for future generations, since the spent fuel could be recovered from the repository to obtain Pu for use in nuclear weapons. The second reason (84) is related to the zircaloy-clad LWR spent fuel rods within metal canisters, which is not a robust waste form for permanent disposal. According to the calculations in support of the Yucca Mountain total System Performance Assessment, the cladding will fail within several hundred to several thousand years. As a result, there could be a large quantity of exposed fuel after permanent closure of the repository. Before reactor-grade Pu can be used in a nuclear weapon, it must be separated from the spent fuel. Plutonium used for such purpose must have a relatively low emission rate of spontaneous fission neutrons, otherwise the probability that the explosive yield will be less than the nominal is increased. Also, Pu used must have a relatively low decay heat generation rate, otherwise a more complex weapon design is required to ensure that thermal limits are not exceeded for structural materials, including the chemical explosive used to initiate implosion. It is expected that the proposed Yucca Mountain repository would contain the spent fuel from irradiation of about 63,000 mt of low-enriched uranium (80). The DOE is proposing to use metal, multi-purpose canisters (MPCs) for use in storage, transportation, and final disposal of spent fuel (85). A practical alternative for the Pu disposal problems is to use RAPD (Reactor/Accelerator/Plutonium Destruction) promising technology (86). Using RAPD, plutonium is converted to plutonium oxide coated particle fuel, which is compacted and placed into graphite fuel elements. After several years of irradiation, the spent graphite fuel elements are an ideal waste form for permanent disposal.

8.6. Concepts of Disposal of Spent Fuels

There are more than 220 mt of highly enriched plutonium (239Pu) in the world (87,88) resulting from the spent nuclear fuel of power plants as well as dismantled warheads. According to the severe environmental impact of Pu, disposal of spent nuclear fuel is the main concern. Disposal concepts of spent fuels have been developed in many countries: USA (89), Canada (90), Sweden (91), Germany (92), and others. In the US and Germany, the disposal concepts are based on the disposal into unsaturated tuff and bedded salt layers, respectively. On the other hand, in Japan, disposal concepts of spent fuels are based on geological conditions while, in Canada and Sweden, the disposal concepts are based on disposal into crystalline bedrock. The Swedish concept, KBS-3, is based on a multi-barrier concept (metallic container-buffer material-geosphere) to protect humans and environment, which is similar to the disposal concepts of several other countries. The spent fuel is assumed to be disposed of in a deep and stable granite rock mass at a depth in the range of 500-1000 m. The repository will be constructed in a stable rock mass not interested by any major fracture. Otherwise, the radionuclides migrate slowly from the repository through the stable rock, and are then transported to the biosphere via a fracture zone (93). One of the most important factors in any repository is the safety of the disposal system. It depends on the performance of engineered barriers (a waste matrix, a container, a
buffer zone, and concrete structures if necessary) to keep radionuclides in the repositories, and the ability of natural barriers to retard and dilute radionuclides during the transport in the geosphere and the biosphere. Different models were developed for safety assessment methodology like, the computer code system GSRW (94) which was developed for the generic safety assessment of geologic disposal of HLW, the source term model, which defines the flux of the radionuclides released from the repository into the surrounding rock formation, and the geosphere model, which calculates the groundwater mediated migration of radionuclides in the homogenous porous media surrounding the repository.

9. Conclusion and Recommendations

One of the more difficult environmental problems is the contamination of groundwater with radionuclides or nonradionuclides. Recently, a limitation of pump-and-treat technologies for decontaminate groundwater have been recognized. One of the most promising technologies for remediation of contaminated sites and design of radioactive waste repositories is the use of permeable reactive barriers (PRBs). PRBs are constructed of reactive material(s) to intercept and remove the radionuclides from the water and decontaminate the plume in situ where, the reactive material(s) is placed in the subsurface between the waste or contaminated area and groundwater (1).

Reactive media used in PRBs should be compatible with the subsurface environment. The media should cause no adverse chemical reactions or byproducts when reacting with constituents in the contaminant plume, and should not act as a possible source of contamination itself. This requires that the chemistry and reactivity of the material be well understood. However, the reactive material should persist over long periods of time and be available at a low to moderate cost. Different categories of reactive barriers have been known: inorganics-sorption barriers, inorganics-precipitation barriers, inorganics-degradation barriers, organic-degradation barriers and organics-sorption barriers (3). The most common barriers used in remediation of groundwater are, hydroxyapatite (and apatite compounds), zero valent iron, and magnesium oxide. When assessing site conditions to determine the feasibility of using a PRB, four general subsurface properties must be measured: plume characteristics, hydrogeology, geochemistry, and microbial activity.

Hydroxyapatite and other apatite minerals have been found effective in immobilizing uranium and other metals through the formation of metal phosphates that are insoluble over a range of chemical conditions (4,5). Apatite is an ideal material over long periods of time because of it’s low water solubility (K_{sp}>10^{-40}), high stability under reducing and oxidizing conditions and over a wide temperature range, availability, and low cost (8,9). The results obtained from X-ray pattern, synchrotron-source XAD, and extended X-ray absorption fine structure spectroscopy (EXAFS) suggest that the predominant U(VI) removal process is complexation by phosphate in the apatite surface (adsorption) (32,33).

Studies have shown that iron based minerals, such as pyrite or magnetite, can effectively adsorb uranium from ground water under favorable conditions (i.e., E_n, pH, dissolved O_2, etc.). They proposed that U^{VI} may be removed from solution by any of three mechanisms: (a) reduction of U^{VI} by ZVI to form the less soluble U^{IV} (i.e., UO_2.xH_2O) phase (anaerobic, anoxic), (b) sorption onto iron oxide corrosion products by ion exchange with hydroxyl sites (aerobic, oxic), or (c) a combination of reduction/precipitation. Sorption, as a removal mechanism, is not preferred because soluble uranium will remain in its more soluble oxidation state, thereby lending itself to be easily transported by the colloidal iron corrosion products. Reduction of U^{VI} to U^{IV} is the preferred removal mechanism since the resulting U^{IV} species is less soluble and thus less mobile in ground water, assuming that the U^{IV} species is not colloidal (35).
Magnesium oxide is used as a backfill material in the Waste Isolation Pilot Plant (WIPP), located at Carlsbad, NM. Magnesium oxides perform several functions to prevent radionuclide migration. First, magnesium oxide reacts with water to form magnesium hydroxide, which maintains the solution pH between 8.5 and 9.5 in WIPP brines. At this pH, actinides have their lowest solubility in WIPP brines. Second, magnesium oxide provides magnesium to complex with organic chelators (oxalic acid, EDTA, citric acid, and acetic acid) in the repository. Otherwise, these organic chelators will complex with the actinides and increase their solubility. The third function of the magnesium oxide backfill is to prevent buildup of carbonate in brines that may contact the waste in the repository and complexes with actinides and increases its solubility (51).

According to the IAEA (57), the radioactive waste is classified into low and intermediate level waste, which may be divided into short lived and long lived waste, and high level waste. While, according to the U.S. standards (58), radioactive waste is classified into six categories, spent nuclear fuel waste, high-level waste, transuranic waste, uranium mill tailing waste, low level waste, and naturally occurring and accelerator produced radioactive materials.

In Egypt, different sources of radioactive waste are present resulting from research activities, radioisotopes production, and radioisotopes application in medicine and industry (59) as well as unwanted radioactive sealed sources. From the characterization of the Inshas site (64-74) as a disposal facility (geomorphology, stratigraphy, meteorology, hydrological analysis, and hydrochemical analysis) together with an inventory of the type and amount of radionuclides present as radioactive waste, we suggest studying hydroxyapatite and zero valent iron in conditioning unwanted radioactive sealed sources, and as a potential backfill material to prevent the migration of radionuclides. However, bench scale laboratory studies, much more information on site characterization and waste forms for disposal is needed before a backfill material can be selected.
10. References

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## Distribution

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