DEVELOPING AND DEPLOYING PERMEABLE ADSORPTIVE LINERS FOR WASTE DISPOSAL

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ABSTRACT

The bench-scale testing and possible deployment of a permeable adsorptive liner (PAL), as a potential alternative to the traditional double-liner system for hazardous, radioactive, and mixed waste landfills, warrants technical consideration for multiple reasons. They include the following:

- Total life-cycle costs should be substantially lower than the standard double-lined system as there will be no leachate to treat and long-term monitoring requirements could be substantially reduced
- Significantly reduces the risk of post-closure vadose zone and groundwater contamination. The method provides a long-term solution, not a short-term band-aid. The permeable adsorptive liner should perform hundreds if not thousands of years, and if properly designed, should far outlast the design life of a standard RCRA liner
- Since there is no leachate to collect and treat, this approach will have a positive impact on any potential ALARA issues
- Validated long-term solutions to low-level and mixed low-level waste disposal should have a positive impact on the regulators and stakeholders for DOE waste disposal program

In the past, the focus for permeable reactive barriers has been in the saturated zone (US DOE, 1998), however, there is no technical obstacle why this same application of contaminant attenuation would not work in the unsaturated zone. Disposal facility trench bottom design can optimize the physical and chemical characteristics of reactive adsorbents in order to maximize artificially-created attenuation for radionuclide and hazardous waste. Disposal sites can optimize PAL design in disposal trench bottoms by adding such reactive materials as flyash, zeolite and other clays, various oxides and zero valence metals (e.g., iron), granulated activated carbon or finely crushed coal (to reduce costs), phosphates, lime, and peat [1]. Once leachate percolates through a reactive, permeable liner, ideally the resultant trench bottom effluent will be "clean." In addition, manipulating the trench-bottom material's pH can also assist in enhancing specific contaminant's retardation.

This same approach of adjusting the pH of percolating water could also be used for landfill covers that are used for "dirty" closure. For example, the solubility of uranium 238 is strongly dependent upon soil pH [2] and in general, the higher the pH, the lower the solubility[2]. Furthermore, phosphates have been demonstrated to retard uranium migration as well [1]. Therefore, if a substantial quantity of a slow-release phosphate ore was installed in a cap overlying uranium waste, the actual uranium migration into an underlying PAL could be substantially reduced. All of these factors can be used to design a landfill cap that can enhance the retardation of the underlying contaminant.

The type and amount of additives, method of additive installation (e.g., layered reactive adsorbents vs. a homogenous blend of adsorbents), thickness of the adsorbents, and physical/chemical manipulations deployed to create an artificial reactive barrier is dependent primarily upon such factors as bench-scale results, waste composition (types and volumes) and climate.

By optimizing the soil adsorption/attenuation processes through various physical and chemical manipulation techniques and minimizing infiltration through the landfill cap, the permeable adsorptive liner could be a safe, viable, long-term alternative to the standard RCRA double-liner system for hazardous, mixed-low-level, and low-level waste disposal. In summary, if permeable reactive liners were shown to be effective in isolating waste, this system would be significantly cheaper to construct than the traditional double-lined system and would provide the ability to isolate waste for thousands of years.

INTRODUCTION

Waste disposal is not only a DOE issue, but also challenges the private sector as well as state and local governments. The bench-scale testing and possible deployment of a permeable adsorptive liner (PAL), as a potential alternative to the traditional double-liner system for hazardous, radioactive, and mixed waste landfills, warrants technical consideration. Permeable reactive barriers in the saturated zone have successfully attenuated organics, metals, and radionuclides at dozens of sites worldwide. In contrast to conventional landfills which are designed to prevent percolation into the underlying vadose zone, the PAL system allows percolation through the reactive media utilizing reactions to prevent or mitigate contaminant fluxes. Any liner system that is installed to prevent the migration of moderate to long-lived radionuclides must be protective for a very long time. The system could be designed to be a stand-alone system or could be used to augment a current double-lined system thereby enhancing the disposal facilities performance assessment.

The following three sequential phases have been proposed in order to field-deploy a field-scale PAL at the Hanford Site:

1. **Phase I** – A U.S. Department of Energy funded Peer Review Panel, composed of technical experts from the national labs, academia, industry, and the regulatory community, met on August 5-6, 2003 to evaluate PAL feasibility and technical merit to develop and deploy permeable adsorptive liners in low-level radioactive waste disposal facilities. Recommendations were made to proceed with Stage II.

2. **Phase II** – Records/data search, current and future waste forms-types and volumes, development of retention technologies for problem contaminants (e.g., technetium-99), modeling, and lab-scale hydraulic, geotechnical, and geochemical testing of the PAL for low-level waste disposal at Hanford would take place. Once the lab-scale testing is concluded, move onto larger-scale pilot tests. The end state of Stage II would be field deployment by the on-site contractor.

3. **Phase III –** Applications of the PAL for mixed low-level waste disposal would be evaluated. Use of the future EPA Permeable Reactive Barrier Research Station (to be constructed near Santa Barbara, CA) would be considered for field scale testing of various PALs for mixed low-level waste. Lorne G. Everett, of Stone and Webster Management Consultants, Inc., is supporting this effort. This stage could take three or more years for testing and regulatory approval.

BACKGROUND

In the past, the focus for permeable reactive barriers has been in the saturated zone [1], however, there is no technical obstacle why this same application of contaminant attenuation would not work in the unsaturated zone. Disposal facility trench bottom design can optimize the physical and chemical characteristics of reactive adsorbents in order to maximize artificially-created attenuation for radionuclide and hazardous waste. Concurrently, a permeable adsorptive liner would avoid the potential "bath-tub" affect from the traditional double-lined systems by permitting the percolation of "clean" water through the trench bottom. Disposal site design can optimize the soil adsorption capacity by artificially creating a

PAL in the trench bottom by adding such materials as flyash, zeolite and other clays, various oxides and zero valence metals (e.g., iron), granulated activated carbon or finely crushed coal (to reduce costs), phosphates, lime, and peat [1]. In addition, manipulating the trench-bottom material's pH can also assist in enhancing specific contaminant's retardation.

This same approach of adjusting the pH of percolating water could also be used for alternate landfill covers that are used for "dirty" closure. For example, a monofill evapotranspiration cap (that allows 2 mm of recharge per year) is used to close a "dirty" site that contains iodine 129 as its primary contaminant, is located in an arid site with alkaline soils. In arid climates with alkaline soils, iodine is predominantly in the iodide and iodate forms. There is a relationship between the high K_d of 129^I and the carbon and nitrogen content of soils [2]. Therefore, certain forms of nitrogen and organic material that are suitable to bind with iodide and iodate could be installed as the initial layer under the landfill cap. Or the addition of minerals containing Cu, Pb, and FeS have been demonstrated to adsorb up to and exceeding 99% of the iodate could also be used as a "polishing" layer underneath the landfill cap [2]. In the case of Technetium-99, if sufficient reducing conditions exist or artificially created, the pertechnetate ion will be reduced to an insoluble oxidation state that are readily sorbed by the soil or form complexes with organic matter and become fixed in the soil[2] . Soils high in organic matter are particularly effective in reducing the pertechnetate ion [2]. In the case of ^{137}Cs, zeolite clays have been demonstrated to remove cesium from solution [2]. For uranium 238, the solubility is strongly dependent upon soil pH [2] and in general, the higher the pH, the lower the solubility [2]. Furthermore, phosphates have been demonstrated to retard uranium migration as well [1]. All of these factors can be used to design a landfill cap used in dirty closures that can enhance the retardation of the underlying contaminant.

Hanford Background

The 1, 450 km^2 (560 mi^2) Hanford Site was acquired by the federal government in 1943 and was dedicated to the production of plutonium for National Security until 1989 when production was terminated. Presently, the Hanford Site is the largest environmental restoration project in the world. The current on-site contractors and sub-contractors manage the treatment, storage and disposal of hazardous (dangerous), radioactive (including low-level, transuranic, and high-level waste streams), and mixed waste streams generated both on the Hanford site and off-site by other generators within the DOE complex authorized to ship waste to Hanford. Hazardous and mixed on-site generated wastes are disposed of on-site at the waste disposal facility called Environmental Restoration Disposal Facility (ERDF) provided at they meet the waste acceptance criteria. ERDF is a RCRA-compliant landfill that is authorized under Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Presently, only waste generated from on-site CERCLA actions can be disposed there. Transuranic waste is stored on site and shipped to the Waste Isolation Pilot Plant in New Mexico for off-site disposal. High-level waste is stored on site, but eventually will be shipped to the Yucca Mountain repository in Nevada for disposal. Low-level waste is treated and stored in permitted facilities and is currently disposed in unlined burial trenches on site. All future low-level waste disposal at Hanford will be conducted at lined trenches in either ERDF expansion cells or the future Integrated Disposal Facility (IDF) which is targeted for Phase I completion by February of 2006.

OVERVIEW OF PERMEABLE ADSORPTIVE LINERS

Permeable adsorptive liners (PALs) are proposed as a potential alternative to the traditional double-lined RCRA compliant systems. The type of media utilized in a PAL design will be based upon current technologies developed from permeable reactive barriers as well as any future materials formulated from research and development activities. The type and amount of additives, method of additive installation (e.g., layered reactive adsorbents vs. a homogenous blend of adsorbents), thickness of the adsorbents, and physical/chemical manipulations deployed to create an artificial reactive barrier is dependent primarily upon such factors as bench-scale results, waste composition (types and volumes) and climate. During bench-scale testing, other issues with the PAL performance may arise including vertical and lateral reactive material migration and load bearing capacities issues (i.e. shear strength) caused by the weight of the waste overburden on the PAL. Engineering design solutions to these potential issues include:

- Specified compaction standards applied during reactive layer installation
- Homogenizing the various materials to avoid the creation of a potential capillary barrier that enhances lateral flow
- Installing specified engineering fabric between layers and anchoring the fabric to the outer perimeter of the waste trench.

Figure 1 illustrates the conceptualization of the PAL system.

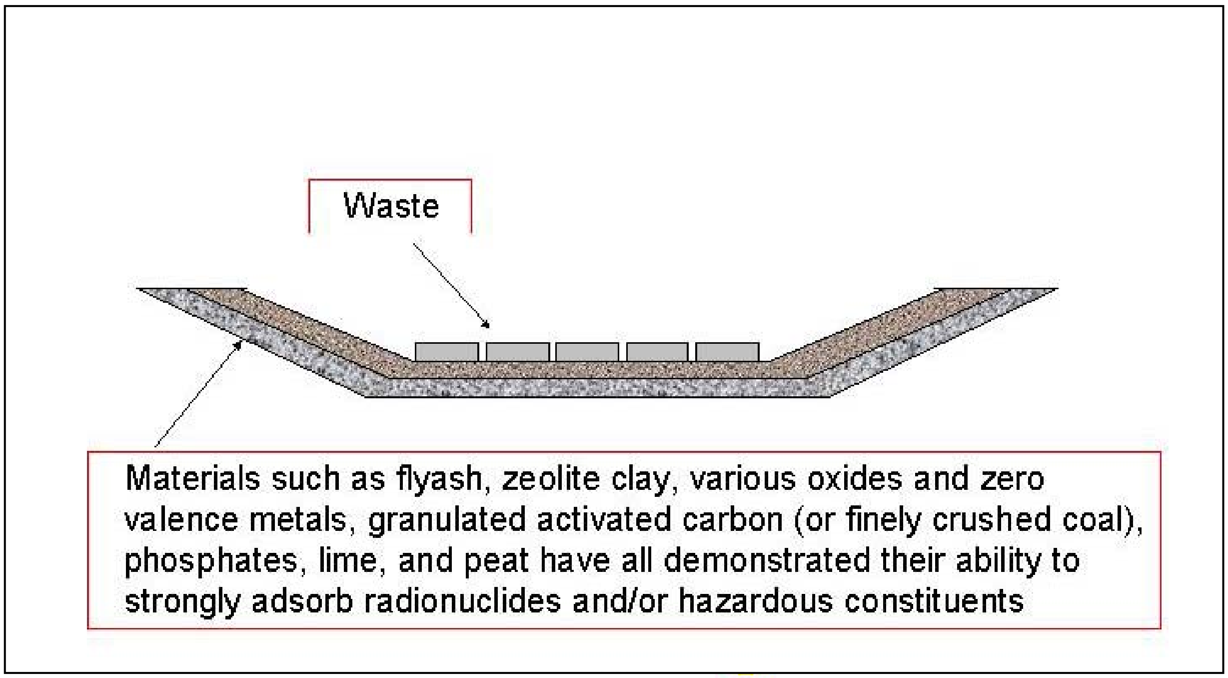

Fig. 1 Permeable adsorptive liner

TECHNICAL FEASIBILITY

Potential Benefits

Deployment of a PAL system could potentially provide some or all of the following benefits:

- Total life-cycle costs for waste disposal will be substantially lower than the standard double-lined system as there will be no leachate to treat, long-term monitoring and maintenance requirements will be substantially reduced
- Increased Performance Assessments for disposal of radioactive waste facilities will be realized and will allow more and/or hotter waste to be disposed at reduced risk

- Significant risk reductions for post-closure vadose zone and groundwater contamination. The method provides a long-term solution, not a short-term band-aid. The permeable adsorptive liner should perform thousands of years provided there is sufficient testing, proper engineering design, and strict construction standards implemented

- Positive impact on reducing worker exposure issues since there will be no leachate to collect and treat

- Validated long-term solutions to low-level and mixed low-level waste disposal will have a positive impact on the regulators and stakeholders for the DOE waste disposal program

- Eliminates the potential "bathtub effect" that could be seen in the traditional double-lined systems caused by lateral moisture flow in stratified soils

- Potential for decreasing the robustness, and therefore costs, of your landfill closure cover

- Potential for lowering landfill construction costs, especially for sites that only require simple adsorbents like flyash and/or zeolite clays

Potential Challenges

Technetium-99 is a very mobile radionuclide that is a ubiquitous waste at the Hanford Site. The development of a cost-effective sequestering agent for technetium is essential for technetium waste disposal. The only other option is waste segregation and separate treatment prior to disposal in a system that will prevent its migration. Presently, the most effective means of immobilizing technetium (VII) is through chemical reduction to Tc (IV). However, this reaction is readily reversible. If the system becomes an oxidizing environment or loses its reduction capacity, Tc-99 can be re-mobilized. Development of a cost-effective sequestering agent for technetium is essential. Apparently there are some preliminary results from Sandia National Laboratory that show some promise with certain materials in immobilizing Tc-99 long-term (Personal communication with Dr. Robert Moore, Sandia, August 6^{th}, 2003).

One of the primary factors for saturated zone permeable reactive barriers (PRBs) failure is problems related to hydraulic capture. Therefore, lessons learned from PRBs should be incorporated into PAL design with such things as layer configuration (e.g., thickness, orientation, homogeneous vs. layered, creation of a capillary barrier, etc), lateral off-site migration of soil-water warranting cut-off walls, and waste packaging design and waste package emplacement. It is critical that the PAL be integrated into the surface barrier and evaluated as a complete system.

Another challenge with PRBs is the declining hydraulic conductivity over time due to such things as mineral precipitation, PAL media consolidation, and void space reductions due to inter-pore deposition of fines. PAL design must take into consideration the above challenges in order to function long-term. For example, PAL media must maintain structural integrity over time despite overburden pressure despite overburden pressure. Structural integrity could be maintained by using engineering fabric between layers, molding the reactive media into porous grains, blocks, or sheets using heat or air entrapment similar to fabricated cinder block. In the case of hydraulics, PAL design needs to carefully consider media residence time and the mitigation of reactive media bypass.

Unsaturated flow model simulations will be required to evaluate the effects of various PAL configurations, surface barriers, and waste characteristics (e.g., waste types, waste package materials, etc.) to evaluate hydraulic as well as geochemical performance. PAL configurations that encourage increased leachate residence times to ensure sufficient contaminant sequestration should also be simulated. Chemical composition of future leachate and the various reactions that take place over time must be modeled. An iterative process of modeling and bench-scale tests should be conducted and results implemented into preliminary deployment of a field-scale PAL. For example, adsorption competition and complexation with native chemical species can change the valence state of dissolved species resulting in adsorption behavior changes. Media transformation is another phenomenon that must be evaluated.

Precipitating species such as metal carbonates, iron hydroxides and oxyhydroxides, metal silicates, and other minerals, can cause coatings on the reactive media resulting in a gradual decline in media reactivity as well as reductions in permeability. However, experience with PRBs has demonstrated that using multiple treatment materials with graded porosities can minimize this problem. The media used to prevent contaminant transport beyond the lower bounds of the reactive liner must be evaluated for compatibility.

There exist computer models suitable for analyzing the PAL system including saturated flow and transport with coupled geochemical reactions including HBGC123[3], OS3D/GIMRT/CRUNCH [4], and RAFT [5]. The appropriate thermodynamic and transport properties need to be either compiled from the literature or measured in the laboratory. These properties include:

- Thermodynamic equilibrium constants for dissolution/precipitation
- Adsorption/desorption
- Redox
- Miscellaneous reactions pertinent to the specific design under consideration
- Kinetic rate constants for all reactions

In addition to the above information, the chemical composition of rainfall as well as water used for dust suppression and compaction of interim landfill covers needs to be collected and input into the various models. Once the data is compiled, the model is designed and preliminary model runs are conducted, data gaps (if they exist) should be identified. Laboratory bench-scale tests should be designed and conducted to reduce parameter uncertainty.

Steps to PAL Deployment

A formal bench-marking exercise, coupled with lessons learned from PRBs, conventional landfills, and vadose zone hydrology and geochemistry provide a significant knowledge base applicable to the research and development of a successful PAL. Phase II of PAL development will essentially focus on the data gaps in our current knowledge base. There are a number of technical issues that warrant additional developmental work in the field of unsaturated zone reactive barriers.

For example, there is a large data-base of existing sorption media that are suited for most of the contaminants at the Hanford Site. However, a comprehensive survey listing the best candidates for Hanford-specific waste as well as a gap-analysis for media that does not exist or has a limited operational life is warranted. Media should be selected based upon a multitude of criteria including performance, costs, expected longevity, and engineering characteristics. In addition, there is a likelihood that new materials must be developed that can immobilize all contaminants of concern that are significant risk drivers for burial ground performance assessment. There is a variety of mechanisms that can be evaluated and enhanced including:

- Adsorption,
- Ion exchange

- Precipitation
- Redox manipulation
- pH manipulation.

Research and development is needed to select the appropriate reactive media that will have a high sorption capacity and be chemically stable over extended periods of time. In Phase II of the PAL development, it is important to ascertain which moderate and long-lived mobile radionuclides and hazardous waste (excluding all heavy metals except Cr^{+6} since they are immobile in alkaline soils) constituents are present at the Hanford Site where the PAL systems will be deployed. Modeling should then be performed to estimate timelines and extent of waste container failure as well as travel times for specific mobile contaminants (present in the inventory) to groundwater or the accessible environment. In addition, the projected waste inventory, container failure, radionuclide half-life and the associated travel times to the underlying aquifer, estimated leachate formed (quantity and quality), and resultant modeling will be the primary factors in developing the reactive barrier used in the sandbox/bench-scale testing.

Once the baseline data has been gathered, sandbox and/or bench-scale model testing should be conducted with the applicable contaminants to evaluate conceptual and analytical model verification and PAL performance. Bench-scale testing could be conducted to evaluate attenuation performance of both the permeable reactive liner for a single, mixed waste mega-trench as well as individual performance of permeable reactive barriers designed to accommodate specific waste-type groupings. Regardless of whether waste segregation would be used or not, a graded approach should still be applied to the PAL design. For example, if your waste disposal trench was designated to accept low-level radioactive waste (excluding most actinides), then a PAL consisting of flyash and zeolite would likely suffice. In contrast, if the designated waste trench was designed to accept a wide variety of mixed wastes, then a more costly, more intricate PAL would have to be designed to properly function. In addition, these experiments will assist in refining the permeable reactive liner design thereby significantly enhancing overall reactive-liner performance as well as designing a system that is ready for field deployment. Testing should include an evaluation of the resultant soil water chemistry after it percolates through the PAL to ensure that there will be no impacts on the underlying vadose zone and groundwater. For example, if the resultant water that percolated through the PAL became too acidic or alkaline, this may cause existing contaminants (if applicable) to mobilize. Therefore, a final layer such as lime or sulfur could be installed as a "finishing" layer to adjust the percolate according to the desired pH.

After the initial bench-scale testing and modeling have been conducted, a risk assessment should be conducted based upon these results. This would include an assessment of such items as expected time of if or when all the reactive liner adsorptive sites would be saturated (if applicable) with contaminants and the resultant slow release of contaminants to the accessible environment taking into account travel times to the groundwater and contaminant dilution in the groundwater/surface water. The risk assessment should include a cost benefit analysis to evaluate what is the maximum acceptable risk (by the regulators and stakeholders) associated with the minimum financial expenditure for PAL design? A potential for reducing the robustness of the landfill closure cover could also be evaluated based upon the results of the PAL tests.

Once there has been a series of successful demonstration of multiple sandbox/bench-scale demonstrations, regulatory and stakeholder acceptance should be paramount. It is critical that the researchers engage the regulators and the stakeholders throughout the entire process. A feasibility analysis of waste separation and subsequent disposal should be completed upon finalization of experimentation, including an overall evaluation of trench-specific attenuation performance, and a cost/benefit analysis of constructing one mixed waste mega-trench versus constructing multiple smaller trenches designed to handle specific waste type mixtures. This evaluation should be conducted as part of the engineering design.

The final step is finalizing the design (or designs) and install your PAL(s) in a trench(es) based upon the information gathered above. This could include an evaluation of installing multiple trenches specifically designed to accommodate specific waste types. If necessary, instrument the trench with performance monitoring (including access ports to evaluate both quality/type and quantity of "leachate" generated) beneath the permeable reactive barrier or install the initial few PAL systems above a double-lined system that includes a leachate collection system for PAL performance validation.

CONCLUSIONS

In summary, if permeable reactive liners were shown to be effective in isolating waste, this system could be significantly cheaper to construct than the traditional double-lined system and may provide the ability to isolate waste for thousands of years. This is in contrast to the uncertainty associated with long-term performance of landfill surface barriers, performance monitoring of the surface barrier, and the long-term performance of the typical composite, double-lined, landfill liner system which have an expected life-expectancy in the hundreds of years range.

The materials used in a RCRA compliant double-lined facility are expected to fail long before the radionuclides have decayed. In contrast, a properly designed PAL could function thousands of years in successfully preventing subsurface migration of hazardous and radioactive constituents. Potential cost reductions in deploying PAL as opposed to the standard double-lined system are due to a variety of factors including:

- Potentially lower construction costs
- The potential for decreasing the robustness and therefore costs of your landfill closure cover
- No leachate to collect and treat during the operating life-cycle of the facility
- Large potential savings in avoiding groundwater or vadose zone contamination and the subsequent, costly remediation
- Potential reductions in long-term monitoring costs
- Overall reductions in total operating time and therefore potentially significant reductions in total lifecycle costs
- Enhanced Performance Assessment resulting in the ability to accept more waste and accept waste that is higher in activity

Ideally, the PAL system could be designed to indefinitely retain contaminants within a cell. Even if the PAL system did not fully function indefinitely, the release of contaminants would be slow and not catastrophic. Although there is support for pursuing the development and testing of PAL systems, the system has not yet been tested and the final designs are unknown at this time[b]. However, by optimizing the soil adsorption/attenuation processes through various physical and chemical manipulation techniques and minimizing infiltration through the landfill cap, the permeable adsorptive liner could be a safe, viable, long-term alternative to the standard RCRA double-liner system for hazardous, mixed-low-level, and low-level waste disposal.

REFERENCES

1 U. S. Department of Energy.1998. *Research and Application of Permeable Reactive Barriers.* Completed under Subcontract No. DE-AC13-96GJ87335 from the U.S. Dept. of Energy, Grand Junction Field Office. Revision 4. April 1998.

2 U. S. Department of Energy. November 1996. *Selected Radionuclides Important to Low-Level Radioactive Waste Management*. DOE publication DOE/LLW-238. Idaho National Engineering Laboratory. National Low-Level Waste Management Program. Lockheed Martin Idaho Technologies Company. Idaho Falls, Idaho 83415.

3 Yeh, G-T, K.M. Salvage, J.P. Gwo, J.M. Zachara and J.E. Szecsody. 1998. *HydroBioGeoChem: A Coupled Model of Hydrologic Transport and Mixed Biogeochemical Kinetic/Equilibrium Reactions in Saturated-Unsaturated Media.* Report ORNL/TM-13668. Oak Ridge National Laboratory, Oak Ridge, TN.

4 Steefel, C.I. and S.B. Yabusaki. 1996. OS3D/GIMRT, *Software for Multicomponent-Multidimensional Reactive Transport: Users' Manual and Programmers Guide*. PNL-11166. Pacific Northwest National Laboratory, Richland, WA. Steefel, C.I. 2001. *GIMRT, Version 1.2: Software for Modeling Multicomponent, Multidimensional Reactive Transport. Users' Guide*. UCRL-MA-143182. Lawrence Livermore National Laboratory, Livermore, CA.

5 Chilakapati, A.S., S. Yabusaki, J. Szecsody and W. MacEvoy. 2000. *Groundwater flow, multicomponent transport and biogeochemistry: Development and application of a coupled process model*. J. Contam. Hydrol., 43, 303-325.

FOOTNOTES

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[b] DOE is in the process of filing a patent for the PAL system. Once final designs are derived for various PAL systems, it is anticipated that additional patents will be filed.

WEBSITES ON PERMEABLE REACTIVE BARRIERS

DOE Grand Junction Office
http://www.doegjpo.com/perm-barr/

DOE Technology Information Center
http://www.em.doe.gov/tie/fall31.html

EnviroMetal Technology Inc.

http://www.beak.com/eti.html

General Electric
http://www.ge.com/cptl/aes/permeable.html

GWRTACT Technical Document
http://www.gwrtac.org/html/tech_status.html

New Mexico Tech
http://griffy.nmt.edu/Hydro/dept/bowman.html

Oregon Graduate Institute
http://cgr.ese.ogi.edu/

Remediation Technology Development Forum
http://www.rtdf.org/barriers.htm

University of Waterloo
http://darcy.uwaterloo.ca/research/categories/rpb.html