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FY 1995 Annual Progress Report from
October 1, 1994 to June 30, 1995

Efficient Separations and Processing Crosscutting Program: Develop and Test Sorbents

L. A. Bray, Principal Investigator

Major Contributors:

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September 1995

Prepared for the U.S. Department of Energy
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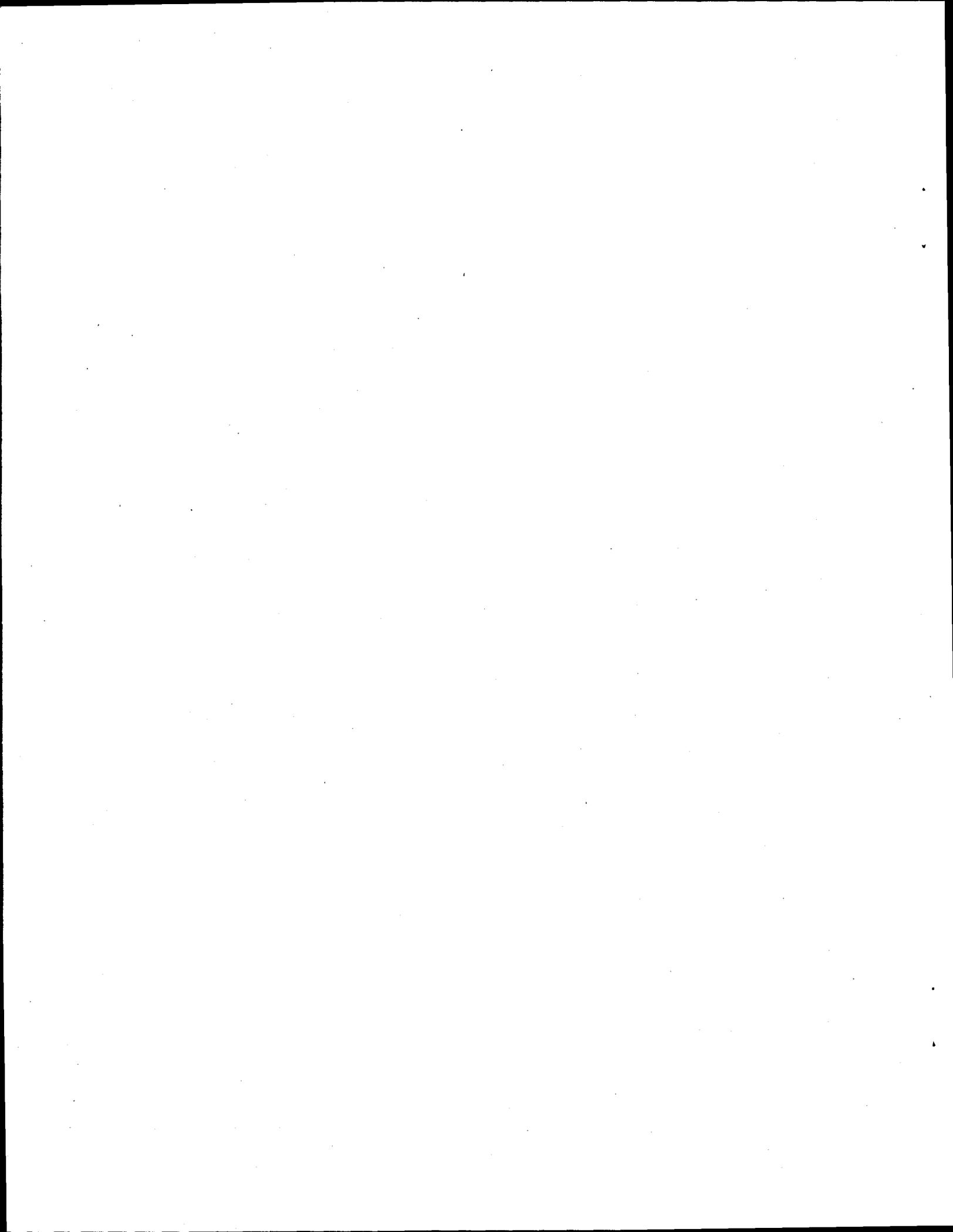
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Executive Summary

This report summarizes work performed during FY 1995 under the task "Develop and Test Sorbents," the purpose of which is to develop high-capacity, selective solid extractants to recover cesium, strontium, and technetium from nuclear wastes. This work is being done for the Efficient Separations and Processing Crosscutting Program (ESP), operated by the U.S. Department of Energy's Office of Environmental Management's Office of Technology Development.

The task is under the direction of staff at Pacific Northwest Laboratory (PNL) with key participation from industrial and university staff at 3M, St. Paul, Minnesota; IBC Advanced Technologies, Inc., American Forks, Utah; AlliedSignal, Inc., Des Plaines, Illinois; and Texas A&M University, College Station, Texas.

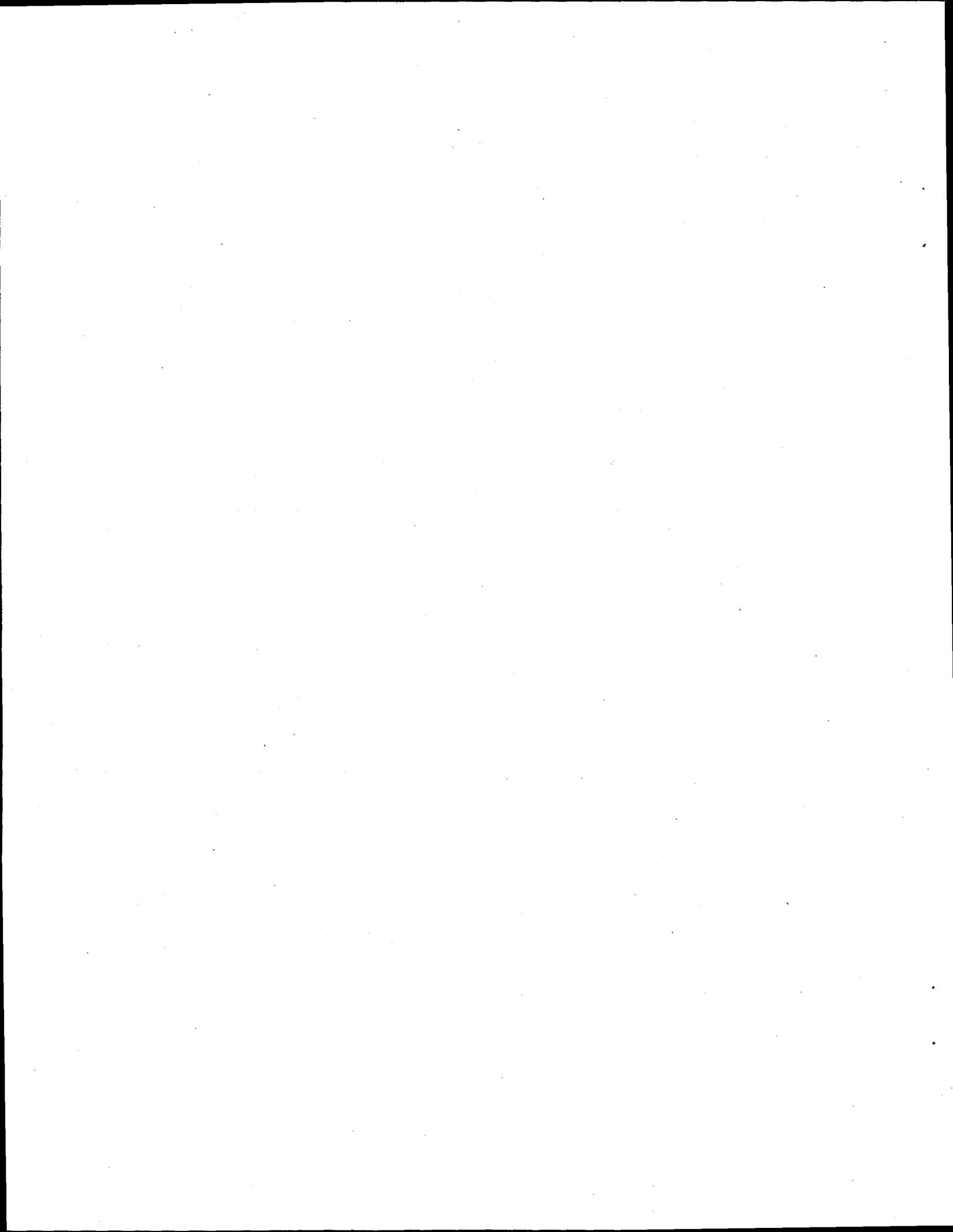
3M and IBC are responsible for ligand and membrane technology development; AlliedSignal and Texas A&M are developing sodium titanate powders; and PNL is testing the materials developed by the industry/university team members.

Major accomplishments for FY 1995 are summarized here.

- IBC SuperLig®644 was tested at 3M using a 200-mL column (20-50 mesh resin). Analysis of three single-cycle loading and elution experiments demonstrated that the IBC SuperLig®644 polymer exhibits the highest cesium capacity per gram of ion exchange material. The cesium capacity (mmol/g) for each resin using Hanford neutralized current acid waste (NCAW) simulant (Na/Cs mole ratio = 1.0×10^4) was calculated to be 0.20, 0.15, and 0.025 for IBC SuperLig®644, resorcinol-formaldehyde (R-F) resin (BSC-210) and CS-100, respectively.
- Batch distribution studies were completed to determine the cesium distribution data for NCAW and double-shell slurry feed (DSSF) as a function of sodium concentration (0.2 to 5 M) using the new SuperLig®644 (20-40 mesh) as compared with R-F, IONSIV®IE-96, powdered CSTs, and CS-100. These synthetic feed results will now be compared with actual Hanford alkaline supernatant. A 200-mL sample of DSSF waste is currently available for testing in the 325B hot cell at PNL. The DSSF waste is a mixture of the supernate from tanks 101-AW (70%), 106-AP (20%), and 102-AP (10%).
- Strontium batch distribution tests with the AlliedSignal bound sodium titanate exchanger were encouraging with K_d s on the order of $400,000 \text{ mL g}^{-1}$.
- 3M and AlliedSignal signed a nondisclosure agreement to share powdered sodium titanate technology for web fabrication and testing. 3M and UOP signed a nondisclosure agreement to share CST technology for web fabrication and testing.

- 3M/PNL/Oak Ridge National Laboratory (ORNL) and 3M/PNL/Westinghouse Savannah River Company (WSRC) held a series of meetings to discuss technical transfer of ion exchange technologies.
- WSRC indicated willingness to investigate AlliedSignal sodium titanate in comparison to Savannah River amorphous monosodium titanate.
- IBC prepared kilogram quantities of SuperLig®644 for testing and web preparation.
- Dr. Vyacheslav M. Abahkin completed his Special American Business Internship Training program at PNL under the direction of Dr. Dennis Wester.
- 3M developed and tested (using rhenium) a test stand for use at West Valley Nuclear Services Co., Inc., for ⁹⁹Tc removal from wastewater at the LLW 02 Treatment facility. A test stand containing a prefilter, two snap-in 3M cartridges (each containing 1 ft² of active surface area) and a post filter in series was fabricated and tested before shipment. The ⁹⁹Tc test stand was attached to the West Valley 02 Facility slip stream (0.1 gpm) on February 14, and tests began. Initial analytical results show excellent chemical performance based on available laboratory ⁹⁹Tc detection limits. The equipment ran for 60 h before a high-pressure drop across the system terminated the test. Additional tests were completed in July.
- Distribution constant measurements were made with strontium exchangers and solutions containing complexants. Among the highlights of this work were that the AlliedSignal strontium exchanger maintains its high selectivity in the presence of complexants such as oxalic or citric acids and EDTA.
- Papers were presented at the 1995 Annual Technical Exchange Meeting in Gaithersburg, MD, January 24-26:
 - "A Historical Overview of Ion Exchange Materials and Delivery Systems for the Recovery of ⁹⁰Sr and ¹³⁷Cs." L. A. Bray, PNL
 - "Evaluation and Comparison of SuperLig®644, Resorcinol-Formaldehyde and CS-100 Ion Exchange Materials for the Removal of Cesium from Simulated Alkaline Supernate." G. N. Brown, L. A. Bray, and R. J. Elovich (PNL); R. L. Bruening and R. M. Decker (IBC); and T. M. Kafka and L. R. White (3M).
 - "Inorganic Ion Exchange for Cesium and Strontium," S. Yates (AS) and A. Clearfield (Texas A&M).
 - "Novel Cesium, Strontium, and Technetium Ion Exchange Membrane," T. M. Kafka (3M) and R. Bruening (IBC)
 - "Design Basis for Metal-Selective Ligands: Molecular Modeling Approach," B. P. Hay (PNL)

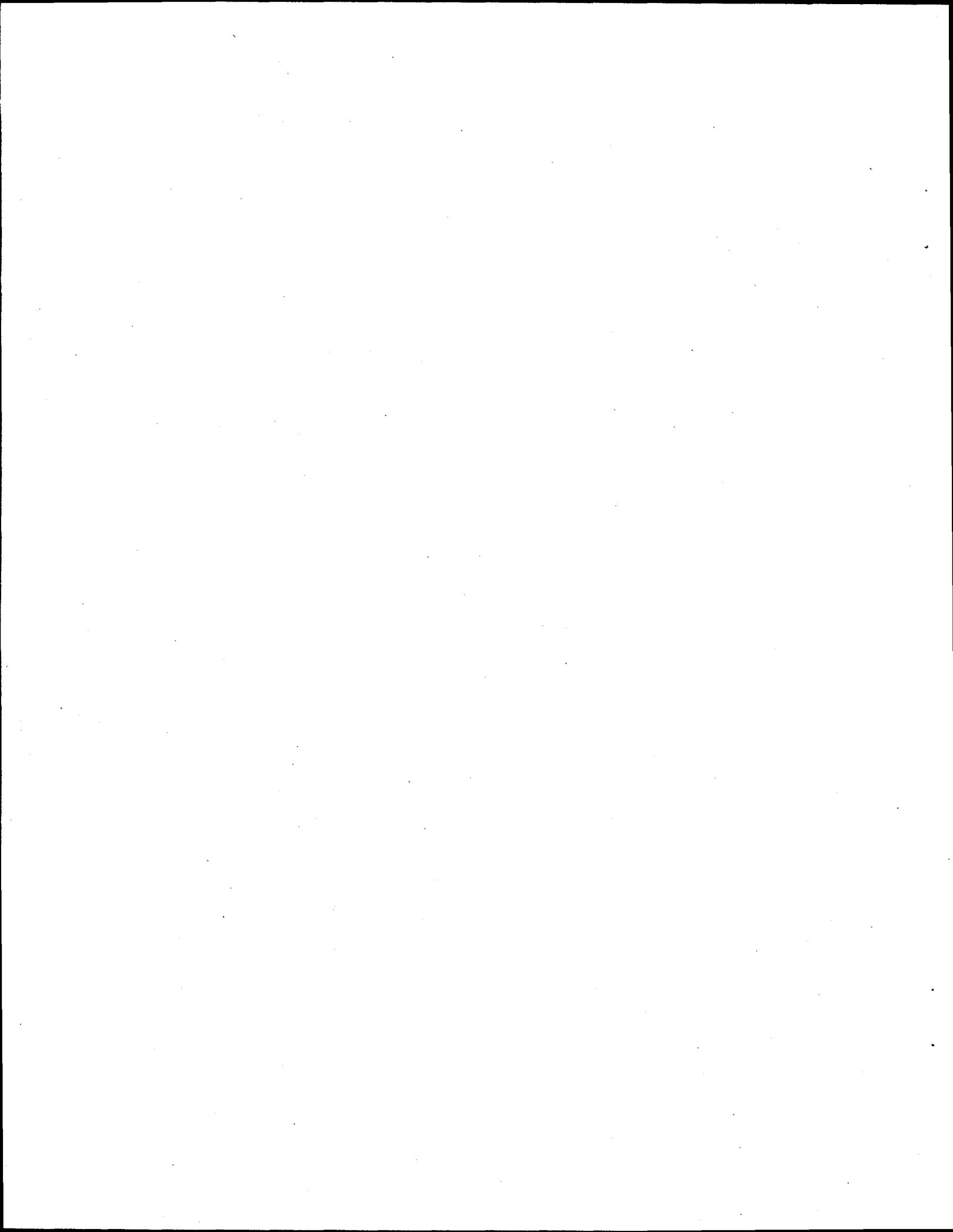
- A proprietary 3M binder was tested and adopted. The binder withstood a ^{60}Co gamma dose of 2×10^9 rad in distilled water over a 6-week period with little or no visible damage.
- Batch strontium K_d values show that the engineered form of the AlliedSignal nonatitanate should be able to equal or better than the performance of the monosodium titanate materials currently used at Savannah River to recover strontium from alkaline tank waste.
- Post-doctoral associate Dr. Delong Zhang arrived at PNL in January to work with Dr. Ben Hay.
- Two PNL documents were distributed describing 1) work completed at Idaho National Engineering Laboratory (INEL) to recover cesium and strontium from acid waste, and 2) the ion exchange performance of SuperLig[®]644 as compared to R-F and CS-100 resins.
- 3M produced and tested Empore[™] membranes containing AlliedSignal sodium titanate powder in 6 M NaNO_3 /0.1 M NaOH containing 60 ppm strontium. Eight hundred membrane volumes of feed were passed before strontium was detected.
- AlliedSignal developed a new phosphate-type ion exchanger based on modification of alkaline titanium phosphates. The granular material has a cesium K_d of 25,000 mL/g from 0.1 M nitric acid. Capacities are expected to be high. Testing and optimization at various acid concentrations is currently under way in anticipation of process scaleup.
- AlliedSignal developed an improved procedure for making sodium titanate into pellets that give improved mechanical strength.
- AlliedSignal inorganic ion exchange powders were requested by Savannah River and 3M. A sophisticated grinding mill has been obtained that can produce fine powders very readily. Preliminary particle size analysis results show that this mill can prepare samples acceptable to 3M.
- Processing trials at 3M resulted in a major advance: uniform carbon-loaded WWL membranes were produced continuously with a 74% carbon loading and 95% particle retention.
- Supplies and a materials list were sent to INEL in preparation for a prefiltration experiment planned using water at TSF-05. Initial experiments were run in preparation for the scale-up of the manufacture of potassium cobaltihexacyanoferrate (PCHF) for use. 20 L of water were sent to PNL to test for ^{137}Cs removal using PCHF. A liter of water was passed through a small PCHF disc to completely remove 1800 pCi Cs/L.



Acknowledgments

The authors gratefully acknowledge the support and encouragement of Dr. T. B. Fryberger, Program Manager, Efficient Separations and Processing Crosscutting Program (ESP) within the U.S. Department of Energy's Office of Environmental Restoration and Waste Management's Office of Technology Development.

The authors also thank PNL staff S. A. Bryan, J. A. Franz, W. L. Shaw, and S. V. Forbes for their work on resin stability; J. R. DesChane, P. K. Tanaka, R. J. Elovich, and C. D. Carlson for their work to provide batch and column distribution data; 3M staff T. M. Kafka, D. Boggs, K. Carlson, T. Fredrickson, D. C. Seeley, and L. R. White for their contribution to web technology; IBC Advanced Technologies, Inc., staff S. R. Izatt, R. L. Bruening, R. H. Decker, G. Mass, and B. Tarbet for their contribution to ligand technology; AlliedSignal staff S. F. Yates, R. Sedath, and I.C.G. DeFilippi for their work on inorganic ion exchange engineering; A. Clearfield and his staff at Texas A&M University, for their help in providing new and emerging inorganic ion exchange materials; and W. L. Kuhn and W. F. Bonner, PNL, for their assistance in program coordination.



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1.0 Introduction

The purpose of this work is to develop high-capacity, selective solid extractants to recover cesium, strontium, and technetium from nuclear wastes for the U.S. Department of Energy's (DOE) Efficient Separations and Processing Crosscutting Program (ESP). To achieve this goal, Pacific Northwest Laboratory (PNL) adopted a broad-based approach that entails identifying and testing candidates for solid-based sequestering agents as well as developing and applying existing materials. A solicitation of interest and capabilities was issued in FY 1992 through Commerce Business Daily to identify candidate industry/ university teams to collaborate with PNL in the proposed studies. Two contracts were awarded: to AlliedSignal, Des Plaines, Illinois, and Texas A&M University on July 1, 1992; and to 3M, St. Paul, Minnesota, and IBC Advanced Technologies (IBC), American Fork, Utah, on November 5, 1992.

This project is designed to test the capacity, selectivity, and stability of selected sequestering agents and substrates in representative physical, chemical, and radiation environments. Emphasis is placed on developing and demonstrating ion exchangers with potential applications in nuclear waste management that would result in major cost reductions and environmental benefits. Although contributions from this task should be useful in addressing a variety of problems in the DOE complex, specific applications at Hanford were initially targeted.

Significant progress was made in FY 1994, including 1) the first successful hot cell demonstration of 3M/IBC technology, which was completed August 1994 at Idaho National Engineering Laboratory (INEL), using WM-185 radioactive acid feed; 2) IBC production of the first sample of a new ion exchange material to remove cesium from pH > 14 waste to the exclusion of potassium; and 3) discovery of a new method for preparing bound sodium titanate, which preserves the high strontium K_{ds} of the original powder and allows the preparation of the engineered form titanate. The binder works at low weight percent, has acceptable mechanical strength, and is resistant to attack by alkali. This represents a major breakthrough in the development of inorganic ion exchangers for use in column operation, under high alkaline waste conditions.

The goals for FY 1995 were to build on the successes of FY 1994 and to continue obtaining the necessary scientific and engineering information required to 1) test and implement ligand-particle web technology; 2) focus on use and commercialization of titanates and mica ion exchangers for the recovery of cesium, strontium, and technetium from acid and alkaline wastes; and 3) complete and apply molecular modeling to ligand design.

The FY 1995 work is divided into three work elements managed by PNL: 1) Technical Coordination and Materials Testing, performed by PNL; 2) Industrial Contracts Support, performed by subcontractors AlliedSignal/Texas A&M and 3M/IBC; and 3) Sorbent Design Support, performed by PNL.

2.0 Industry Partnership

Technology for selective removal of contaminants from DOE high-level waste and wastewater is being developed and successfully deployed by the PNL Industry/National Laboratory partnership. This partnership arrangement can be a model for effectively and efficiently bringing industry and national laboratory staff together to solve DOE waste remediation needs. Interfacing with industry in this manner provides

- application of industrial technology to DOE needs
- transfer of knowledge of DOE needs from national labs to industry
- management of technology development/adaptation by experts in the field
- entrepreneurial spirit of industry focused on DOE needs.

2.1 Background

Congress has determined that the remediation of the DOE waste legacy will be performed by industry under DOE's direction. Technology developed for this purpose must, therefore, include industry as early as possible. A team of PNL scientists and industry representatives has been highly successful in converting industrial expertise into solutions for DOE waste needs. A description of this emerging collaborative relationship follows.

2.2 Team Formation and Operation

Responding to needs identified at several DOE sites, in 1992 PNL contracted with industrial partners to assist in development and deployment of technologies to remove contaminants from DOE wastes. 3M, St. Paul, Minnesota, and IBC Advanced Technologies, Inc., American Fork, Utah, have an appropriate mix of sorbents development expertise coupled with the ability to engineer the sorbent into an engineered form capable of being deployed in a cartridge for ease in waste cleanup operations. AlliedSignal (AS), Inc., Des Plaines, Illinois, in partnership with Texas A&M University, are screening and developing solid inorganic ion exchangers to recover cesium and strontium from nuclear alkaline and acid wastes.

Under the direction of experts in the sorbents field who were also familiar with separations technology needs at DOE sites, a membrane-based sorbent system and other inorganic and organic ion exchange materials were developed that are directly applicable to DOE needs. A team was organized that through careful application of industry expertise coupled with knowledge of DOE needs and constraints, has developed sorbents with uniquely applicable properties. Development of the organic

resins, inorganic exchangers, and membrane systems in the industrial/university laboratories followed by testing against competing products, often with actual radioactive wastes at PNL, has provided an efficient development path.

Under contractor tutelage, the industrial partners have quickly learned DOE needs, constraints, policies, and methods of business; and the 3M/IBC and AS/Texas A&M staffs have become knowledgeable about DOE needs through DOE and contractor personnel at several sites. The subcontracts have been worded to encourage aggressive interface with DOE sites. In turn, the sites all responded with waste streams they wanted addressed. There has been a more positive response from the sites when the industrial/university partners present our case rather than PNL, a competing lab, promoting the technology.

2.3 Technical Accomplishments

Sorbents have been developed and tested that are uniquely applicable to DOE needs for both groundwater and high-level waste applications. The ion exchange sorbents have been incorporated into a web structure that provides selective ion removal without the disadvantages of a large ion exchange column system. The web can be placed in a cartridge and either disposed when loaded or the captured contaminants can be eluted and the web reused. Organic and inorganic ion exchange materials are being tested at selected sites.

2.4 Demonstrations/Implementation

Because PNL's transfer of knowledge regarding technical needs to industry, a number of demonstrations and plans for implementation were made possible. After being shown the applications to which the sorbents technology is most applicable, industry has made a number of contacts, and as a team the following demonstrations have been planned or completed.

- **INEL High-Level Waste.** A test performed in the INEL analytical hot cell demonstrated the ability of titanium phosphate ion exchange and IBC SuperLig[®]620, placed in a 3M web, to recover ¹³⁷Cs and ⁹⁰Sr from actual high-level acid waste.
- **West Valley Demonstration Project Effluent.** A pilot-scale demonstration of ⁹⁹Tc removal from plant effluent is being conducted at West Valley, New York. During this test, a 0.1-gpm sidestream of plant effluent flows through a skid-mounted unit containing snap-in 3M cartridges each containing 1 ft² of active surface. Equipment installation/setup, operations, sampling, and primary sample analysis is provided by onsite EM-30 operating staff. On successful completion of testing, the West Valley Demonstration Project plans to purchase larger cartridges for treatment of the full effluent stream. This will be the first direct transfer of ESP-developed technology to EM-30.

- **INEL Test Area North 05 Injection Well.** The removal of both ^{90}Sr and ^{137}Cs from groundwater at the INEL Test Area North (TAN) Injection Well 5 is being planned for demonstration this summer. Although all decisions are not made yet, it was agreed that the costs to set up the skid unit at TAN, operations during the testing, sampling, and onsite analysis would be borne by the EM-30 operations contractor, LITCO, if EM-50 would pre-test the unit at PNL with samples of TAN water, bring the unit to INEL and provide oversight during operation.
- **Hanford High-Level Waste.** Meetings were held with DOE-RL, PNL, 3M, Westinghouse Hanford Company (WHC) engineering, and WHC evaporator operations to initiate a study evaluating the options and costs of demonstrating removal of ^{137}Cs from actual Hanford high-level waste using the 242-A Evaporator building. The PNL/3M team will work closely with WHC engineering to prepare the unit for radioactive demonstration, and the WHC evaporator operating team will provide operations.
- **Hanford Groundwater.** Hanford operating personnel from CH2M, Bechtel, and IT met with PNL and 3M staff to review joint interest in sorbent demonstrations for the 200-UP-1 and BP-5 operable units' contaminated groundwater. A demonstration of removal of strontium, cesium, technetium, uranium, chromate and other species from the groundwater was requested.
- **ORNL Melton Valley Waste.** Oak Ridge National Laboratory (ORNL) staff are preparing to test 3M/IBC SuperLig[®]644 both in the 20-40 mesh ion exchange column form and in the web form using actual alkaline Melton Valley Storage Tank waste. PNL/3M/IBC will prepare the ion exchange materials to be tested, pretest the materials using synthetic feeds and ^{137}Cs radiotracer, and share in the performance of the actual test.

2.5 Conclusion

The "Partnership Model" arrangement has been used effectively and efficiently to bring industry and national laboratory staff together to solve DOE waste remediation needs. Interfacing a National Laboratory such as PNL with industry in this manner provides a link in solving DOE needs. It shortens the learning time, strengthens the management of new technology development, and facilitates the deployment of new products by experts in the field. It also infuses the entrepreneurial spirit of industry focused on DOE needs, with an industry requirement to enter the market with a profitable and successful product.

The following sections briefly describe the work performed by the PNL team, the 3M/IBC team, and the AS/A&M team. The work completed on modeling by B. P. Hay, PNL, is described in a separate annual report.

3.0 Technical Coordination and Materials Testing

(L. A. Bray and G. N. Brown, PNL)

Ion exchange samples are being tested at PNL using simulated and actual wastes. Filter cartridge, ion exchange material, and batch distribution tests will continue when appropriate. Radiation testing of selected materials will continue. Samples of 3M webs, AS sodium titanates, and Sandia National Laboratories (SNL) crystalline silicotitanates (CSTs) will be tested as a function of pH and radiation stability. Concerns for binder and web radiation and chemical stability will continue to be addressed.

PNL has continued to develop a series of batch distribution tests to compare ion exchange materials over the pH range using a 5 M sodium ($\text{NO}_3^- - \text{OH}^-$) solution and 0.0005 M cesium or strontium and synthetic neutralized current acid waste (NCAW) and double-shell slurry feed (DSSF) alkaline waste feeds (0.2 to 7 M Na^+ and Na/Cs mole ratios of 50 to 500,000). Sandia's CSTs (UOP Molecular Sieves, Mt. Laurel, New Jersey), Savannah River resorcinol-formaldehyde (R-F) resins (Boulder Scientific, Mead, Colorado), phenolic CS-100 (Rohm and Haas, Philadelphia, Pennsylvania), sodium titanates (AS), and SuperLig[®] ion recognition materials (IBC Advanced Technologies, Inc.) are examples of the exchangers being evaluated. This information provides a uniform basis for comparison. In addition, as AS and 3M/IBC materials become available, radiation stability testing using the ⁶⁰Co facility is being employed.

3.1 Idaho National Engineering Laboratory Hot Cell Test

The first opportunity to test 3M/IBC systems with actual radioactive waste was successfully completed at INEL using acid radioactive waste containing both ¹³⁷Cs and ⁹⁰Sr. Synthetic "mimic" wastes were used to test the system both at the 3M laboratory as well as at INEL before the actual hot cell test. Results from those tests were confirmed in actual waste testing. The experience provided 3M/IBC/INEL/PNL staff an opportunity to work as a team to obtain a satisfactory technical solution for a major waste stream. A formal PNL report provides the details of the completed work (Bray et al. 1995). Additional opportunities to demonstrate AS and 3M exchangers are being investigated.

3.2 Idaho National Engineering Laboratory Test Area North 05 Injection Well

PNL scientists completed a successful laboratory test demonstrating the removal of ¹³⁷Cs from INEL Test Area North (TAN) groundwater. Receiving a 20-L sample of TSF-05 water from INEL for testing, the PNL analytical laboratory confirmed a ¹³⁷Cs content of approximately 1800 pCi/L. A liter of the water was passed through a 1-in.-diameter 3M disc containing potassium cobaltihexacyanoferrate

(PCHF), after which the water was recounted. The ^{137}Cs was below detection limit of < 7 pCi/L. The disc contained 1800 pCi. Based on this test, plans are continuing for onsite testing for cesium removal from INEL TAN groundwater this summer.

3.3 Ion Exchange Column Testing

G. N. Brown and R. J. Elovich completed a series of cesium ion exchange removal experiments using PNL-designed and constructed columns (200-mL capacity) in conjunction with 3M's New Products Department. Representatives from PNL, 3M, and IBC defined, modified, and conducted the column ion exchange procedures required to remove cesium from a large volume (60 L) of simulated Hanford NCAW. The objective of the experiment was to compare three ion exchange materials—IBC SuperLig[®]644, Boulder Scientific R-F (BSC-210) and Rohm and Haas CS-100—in a side-by-side analysis and to provide a baseline of column results from which later Empore[™] membrane SuperLig[®]644 cartridge data could be evaluated. Each material was tested by loading a single 200-mL column with NCAW simulant (Na/Cs mole ratio = 10^4) at 1800 mL/h (9 column volumes [cv]) at 25°C. Elution was completed using 0.5 M HNO_3 at 200 mL/h (1 cv/h) at 25°C.

A PNL formal report was completed (Brown et al. 1995), and the following conclusions were developed.

- Analysis of these single-cycle loading and elution experiments demonstrates that the SuperLig[®]644 polymer exhibits the highest cesium capacity per gram of ion exchange material in NCAW and the greatest volume compression on acid elution with 0.5 M HNO_3 . Because of the relatively high density and poor elution, BSC-210 exhibits the highest cesium capacity per unit volume of ion exchange material and a lower volume compression. CS-100, the baseline material for cesium ion exchange at Hanford, was found to be inferior to either SuperLig[®]644 or BSC-210 in terms of cesium capacity and selectivity over sodium.
- The cesium capacity (mmol/g) for each resin using Hanford NCAW simulant (Na/Cs mole ratio = 1.0×10^4) was calculated to be 0.20, 0.15, and 0.025 for SuperLig[®]644, BSC-210, and CS-100, respectively.
- The cesium capacity (mmol/mL) for each resin using Hanford NCAW simulant was calculated to be 0.047, 0.070, and 0.013 for SuperLig[®]644, BSC-210, and CS-100, respectively. The total column volumes of NCAW simulant required by the 200-mL column to achieve 0.5 C/C_0 was 93 (19 L), 140 (28 L), and 25 (5 L) for SuperLig[®]644, BSC-210, and CS-100, respectively.
- Elution of each resin material with 0.5 M HNO_3 required 3.5 (0.70 L), 7.0 (1.4 L), and 3.6 cv (0.72 L) to reach 0.1 C/C_0 for SuperLig[®]644, BSC-210, and CS-100, respectively. This resulted in a volume compression of 27, 20, and 6.9.

- The peak concentration achieved during the elution process was determined to be 185 C/C₀ (12 g Cs/L), 38.5 C/C₀ (2.5 g Cs/L), and 27.8 C/C₀ (1.8 g Cs/L) for SuperLig®644, BSC-210, and CS-100, respectively.
- The cesium mass balances based on analysis of the column loading and elution effluent composite solutions were calculated to be 105%, 90%, and 98% for SuperLig®644, BSC-210, and CS-100, respectively.
- Before the pretreatment process, the NCAW simulant feed exhibited a Na/Cs mole ratio of 10,000 and a K/Cs mole ratio of 240. The composite elution effluent from the fully loaded ion exchange column exhibited a Na/Cs mole ratio of 10.5, 20.6, and 78.2 and a K/Cs mole ratio of <0.046, 0.136, and 0.160 for SuperLig®644, BSC-210, and CS-100, respectively.

3.4 Batch Distribution Studies

Batch distribution studies were initiated to determine the cesium distribution data for NCAW as a function of sodium concentration (0.2 to 5 M) using the new SuperLig®644 (20-40 mesh) as compared with R-F, IONSIV®IE-96 (UOP), powdered CSTs (IONSIV®IE-910), and CS-100. Batch distributions as a function of temperature (10°C, 25°C, and 40°C), sodium concentration (0.2, 1, 3, and 5 M Na⁺), at equilibrium Na/Cs mole ratios from 10³ to >10⁷, were completed for SuperLig®644 (Figures 3.1 - 3.4). This new ion exchange resin can now be compared to IE-96, CS-100, R-F, and powdered CST DG-112 (an early research form of IE-910 powder) on the same basis (Figure 3.5). These results show that, as expected, powdered CSTs and R-F provide higher values ($\lambda = \rho \times Cs K_d$, where ρ = bed density determined in 2 M NaOH) than IBC SuperLig®644 using NCAW (Na/K mole ratio = 43). The results also illustrate similar cesium loading data (at C/Co = 0.5) as that reported for 3M column loading (200 mL). The other important discovery is that the SuperLig®644 cesium K_d values drop off rapidly in <pH 13 feed. This should allow elution of the loaded cesium SuperLig®644 resin at pH values of ~7 (Figure 3.6).

This work is currently being repeated using simulated and actual Hanford DSSF at 25°C. The tests will include preliminary testing of the best currently available ion exchange materials (powder or engineered form). The K_d values will be determined for cesium (0.2, 1, 3, 5 M Na⁺), and strontium and plutonium at 5 M Na⁺. A 200-mL sample of mixed DSSF waste has been provided by WHC, and the sample is currently in the 325B hot cell. The DSSF waste is a mixture of the supernate from tanks 101-AW (70%), 106-AP (20%), and 102-AP (10%). Based on the WHC analytical results, synthetic DSSF waste was prepared and traced with ¹³⁷Cs, ⁸⁵Sr, or ²³⁹Pu. Batch distribution tests were completed using the selected exchangers and synthetic DSSF to provide a baseline for comparison with the actual waste solutions and to optimize the radiochemical experimental conditions (Figures 3.7 - 3.11). The exchangers were then compared using DSSF and an equilibrium Na/Cs mole ratio of 10⁴ on the same basis (Figure 3.12). Batch distribution tests will then be performed using actual Hanford DSSF and selected exchangers.

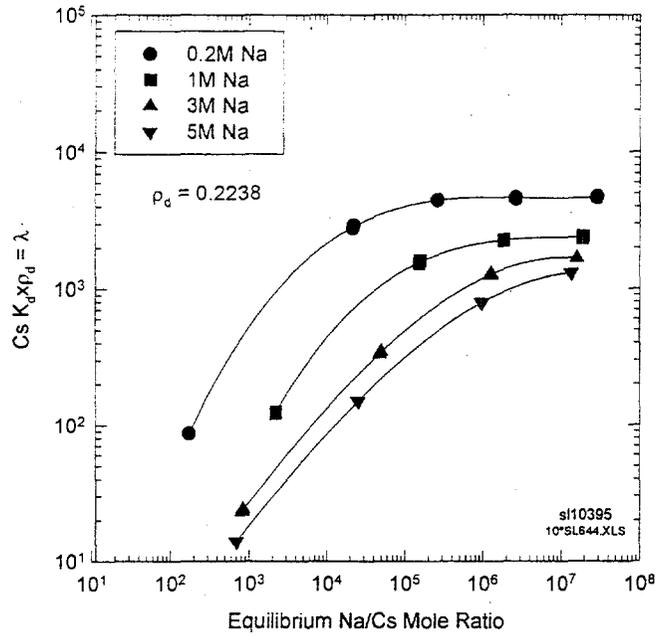


Figure 3.1. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 10°C, for NCAW and SuperLig®644

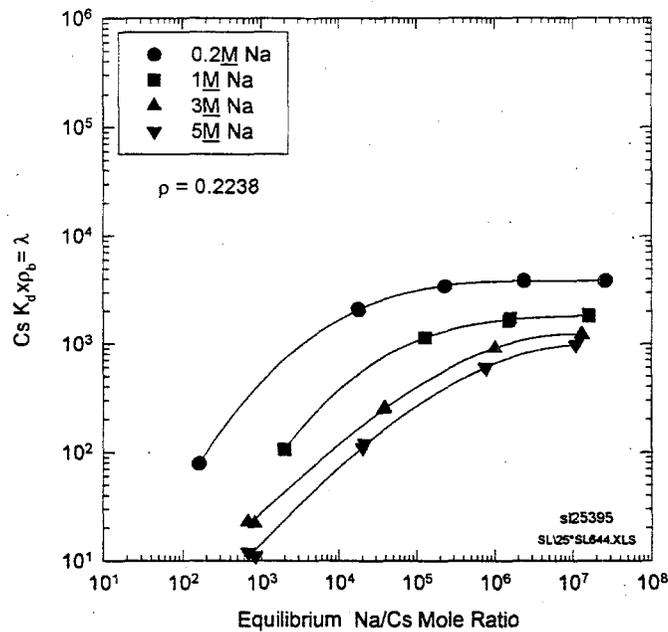


Figure 3.2. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 25°C, for NCAW and SuperLig®644

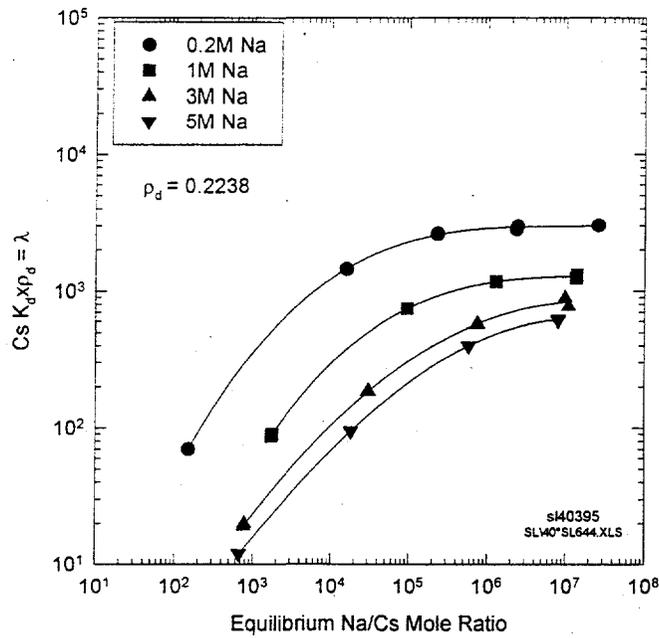


Figure 3.3. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 40°C, for NCAW and SuperLig®644

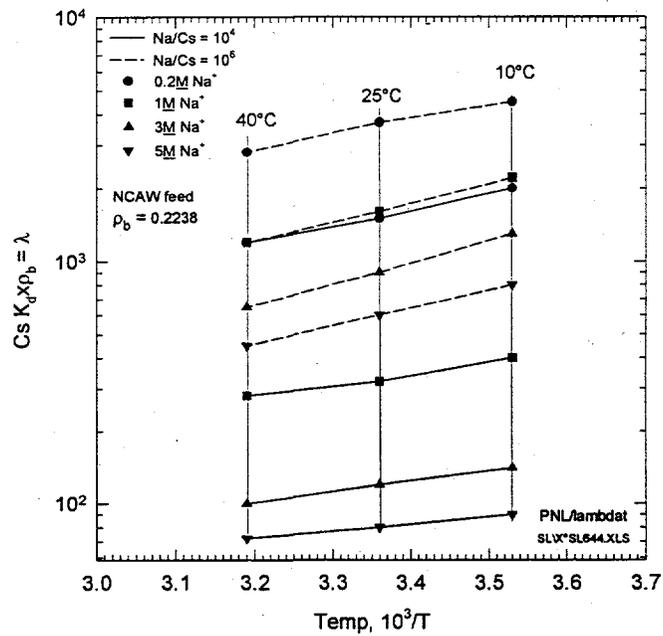


Figure 3.4. Cesium Distribution as a Function of Temperature

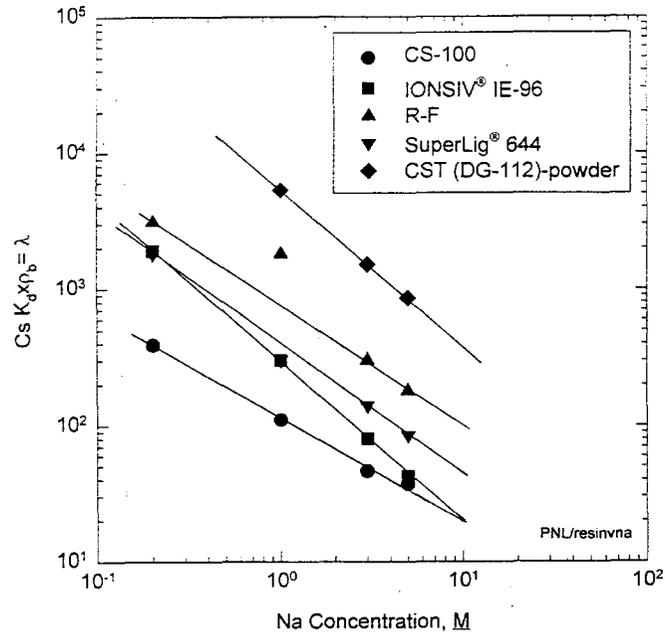


Figure 3.5. Cesium Distribution as a Function of Sodium Concentration, 25°C, for NCAW and Five Exchangers

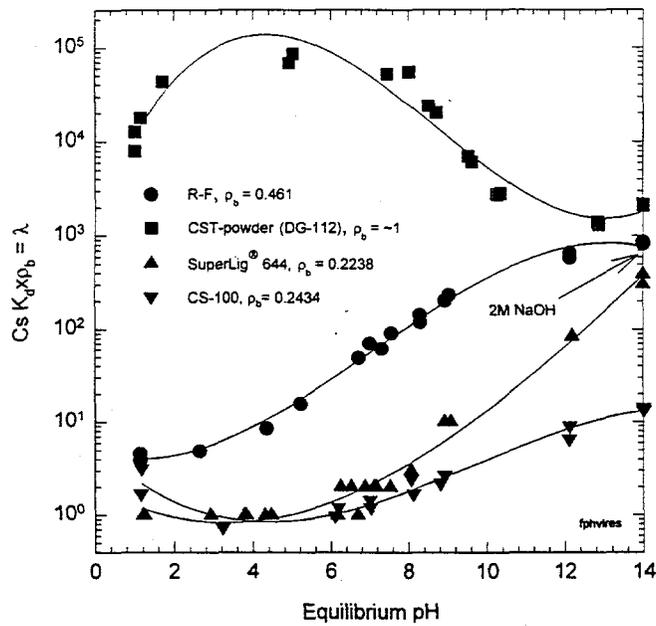


Figure 3.6. Cesium Distribution as a Function of Equilibrium pH, 25°C, for 5 M Na⁺ and 5 x 10⁻⁴ M Cs⁺

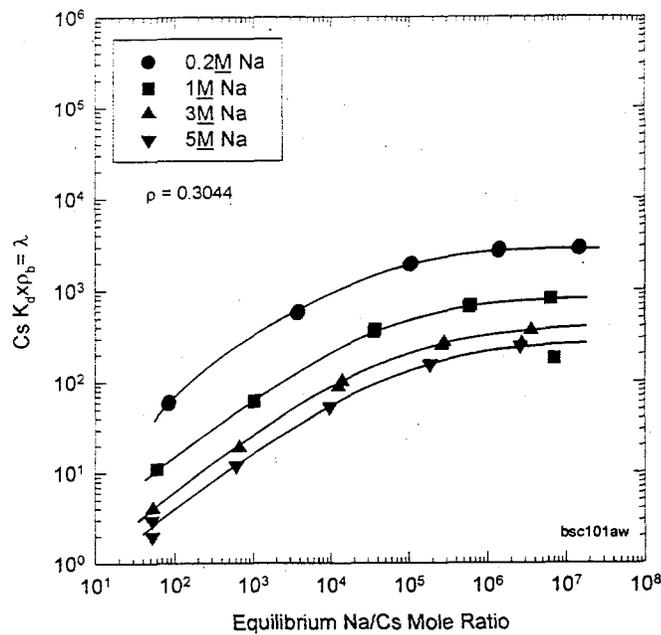


Figure 3.7. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 25°C, for DSSF and R-F Resin (BCS-210)

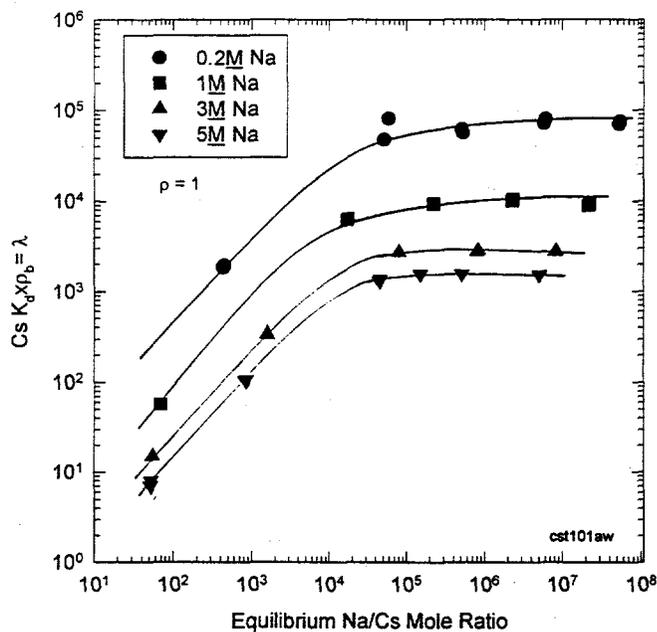


Figure 3.8. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 25°C, for DSSF and IONSIV®IE-910

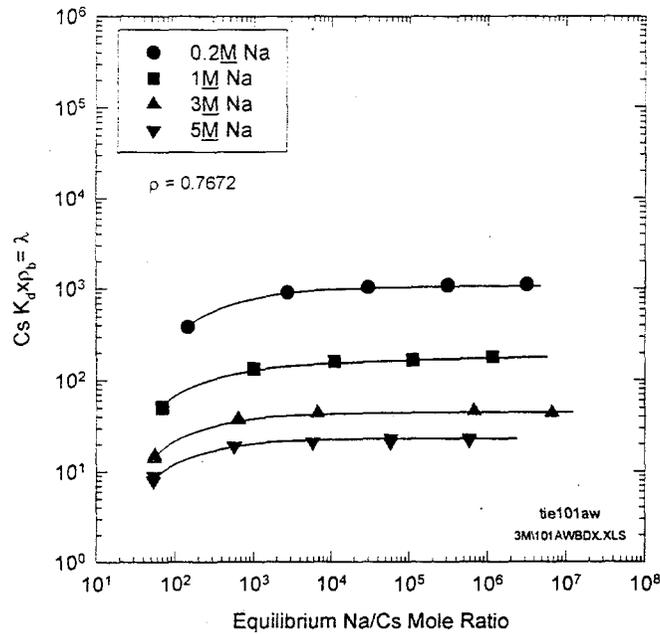


Figure 3.9. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 25°C, for DSSF and IONSIV®TIE-96

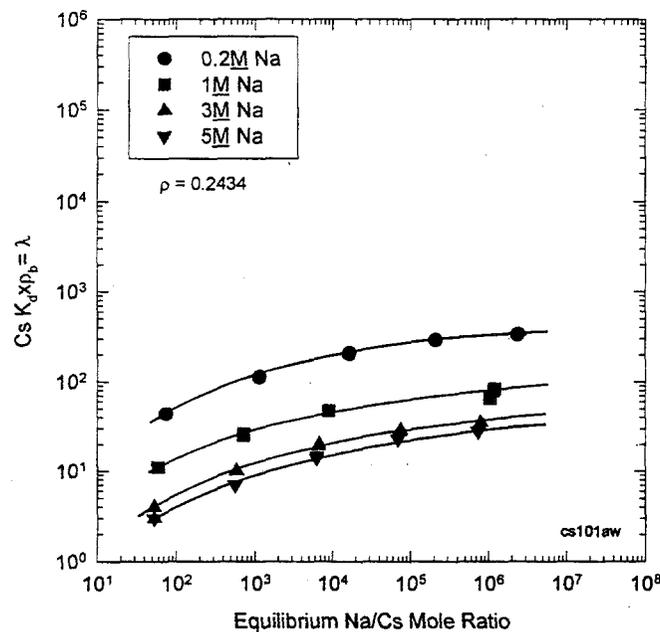


Figure 3.10. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 25°C, for DSSF and CS-100

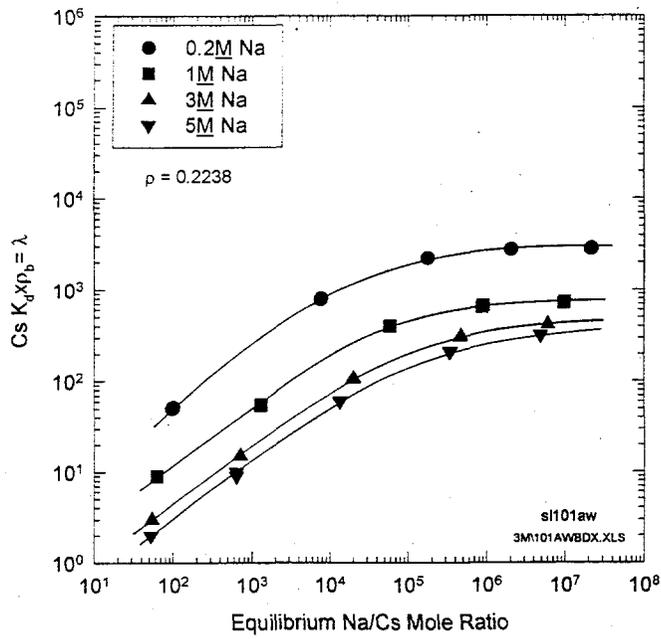


Figure 3.11. Cesium Distribution as a Function of Equilibrium Na/Cs Mole Ratio, 25°C, for DSSF and SuperLig®644

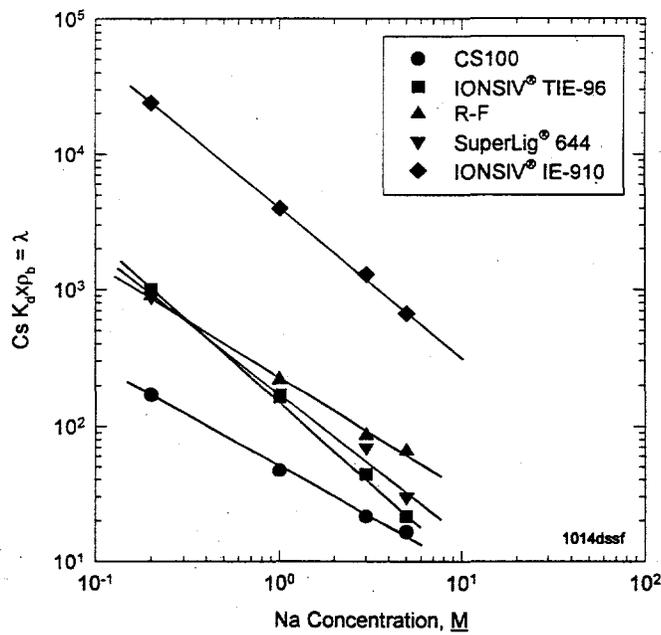


Figure 3.12. Cesium Distribution as a Function of Sodium Concentration, 25°C, for DSSF and Five Exchangers

3.5 Stability of Organic Ion Exchange Resins

IBC is developing a new class of sequestering agents (SuperLig®) that can selectively remove various radionuclides (cesium, strontium, etc.) from high ionic-strength alkaline solutions based on molecular recognition technology. Previous tests have demonstrated that one of these materials (SuperLig®644) can remove cesium from simulated Hanford tank waste even in the presence of excess sodium and potassium (Brown et al. 1995). To more accurately assess the potential use of this technology for the pretreatment of nuclear process wastes, the oxidative and radiolytic stability of SuperLig®644 was tested and compared to that of two current baseline materials (R-F and CS-100).

The radiation stability of each resin was determined by exposing the materials to ⁶⁰Co gamma radiation and measuring the evolved gases. A small subsample of each resin was removed after each exposure period and analyzed for cesium selectivity by K_d analysis. Stability towards oxidation was determined by O₂ uptake measurements, structural analysis by NMR, and cesium selectivity by K_d analysis after each oxygen exposure.

The results demonstrate for the first time the stability of the newly produced SuperLig®644 with a direct comparison to two other organic ion exchangers. In general, the SuperLig®644 is less stable toward oxidative and radiolytic degradation than either the R-F or CS-100 resins.

The following specific conclusions and recommendations resulted from the study.

- Following irradiation, all materials tested demonstrated a decrease in cesium selectivity and capacity. The cesium λ value in NCAW decreased by a factor of two to six after exposure to 1.0E+09 rad. The relative stability roughly follows the order CS-100 > R-F > SuperLig®644.
- Oxygen uptake measurements indicate the relative instability of SuperLig®644 compared to R-F. In 1 M NaOH and NCAW, initial O₂ uptake was 17.4 and 7.38 mL O₂ g⁻¹ h⁻¹ for SuperLig®644. In contrast, the oxygen uptake by R-F in the same solutions was 7.50 and 4.22 mL O₂ g⁻¹ h⁻¹, respectively.
- The cesium λ values for SuperLig®644 decreased from 400 to 5 and 30 after 16-h exposure to O₂ in 1 M NaOH and NCAW, respectively.
- During the irradiation of SuperLig®644, R-F, and CS-100 in a simulated NCAW matrix, the following gases (listed by decreasing abundance) were generated: hydrogen, nitrous oxide, nitrogen, and oxygen. The relative amount of these gases produced is consistent with the organic resin material acting as a source of reductant within the system. The irradiated SuperLig®644 evolved more H₂, N₂O, and N₂ and less O₂ than either the R-F or CS-100 resins, indicating the relative instability of the former compared to the latter.

- Analysis of the SuperLig®644 by NMR spectroscopy before and after exposure to oxygen indicated extensive modification of the overall chemical structure during degradation. The data demonstrate the utility of using spectroscopic methods for monitoring changes in the chemical structure of organic resins during oxidation and/or radiolysis.

The data are self-consistent and indicate the relative stability of three organic polymers (CS-100 > R-F > SuperLig®644) under a variety of chemical and radiolytic conditions. The materials are currently being considered for use in the cesium ion exchange pretreatment of Hanford tank wastes. It should be noted that the most stable material (CS-100) exhibits the worst cesium loading performance. All three materials appear to be sufficiently stable for cesium ion exchange processes in alkaline supernates up to $1.0E+08$ rad cumulative exposure.

3.5.1 Oxygen Uptake Measurements

Oxidation of SuperLig®644 and R-F was completed under static conditions and involved exposing each resin material to one atmosphere of pure oxygen at room temperature within a sealed reaction vessel. The sealed system allowed convenient measurement of resin oxygen uptake by direct correlation with the total reaction vessel pressure. An important assumption during the test was that the resin was only partially oxidized (e.g., formation of ketone, aldehyde, carboxylic acid functional groups, etc.) and did not generate any gaseous species (e.g., carbon dioxide) that might increase the reaction vessel pressure. In addition to these oxygen uptake measurements, the resin degradation as a function of time was evaluated by NMR spectroscopic analysis of the resin and by cesium batch distribution (K_d) measurements.

During the oxidation process, between 0.8 and 1.3 g of each resin was separately suspended in 100 mL of either 1 M NaOH or the aqueous NCAW simulant solution. Before initiating the oxidation experiments, the apparatus was evacuated and purged a minimum of three times with pure oxygen. The sample flask was attached to the vacuum line and purged with pure oxygen for 15 min. The system pressure was increased to atmospheric pressure with O_2 . The pressure in the sample flask as a function of time was measured with a manometer and kept constant by continuously adjusting the elevation of the manometer. After oxidation, the solid samples were separated from the liquid by vacuum filtration and saved for additional NMR and cesium K_d analysis.

Oxygen Uptake - The uptake of oxygen by the SuperLig®644 and R-F resins in a simulated NCAW supernate and 1 M NaOH solution was investigated over the course of 16 h. The data are displayed in Figure 3.13 and show the relative stability of the R-F over the SuperLig®644. In both solutions (NCAW and NaOH), the magnitude of initial O_2 uptake for the SuperLig®644 is approximately twice that of R-F. For both materials the O_2 uptake is greater in 1 M NaOH than in NCAW. The reason for this difference is currently unknown but may be related to relative oxygen solubility in the two solutions. This could also be caused by chemical interactions associated with additional species in the NCAW (e.g., NO_3^- , NO_2^- , $Al(OH)_4^-$, etc.).

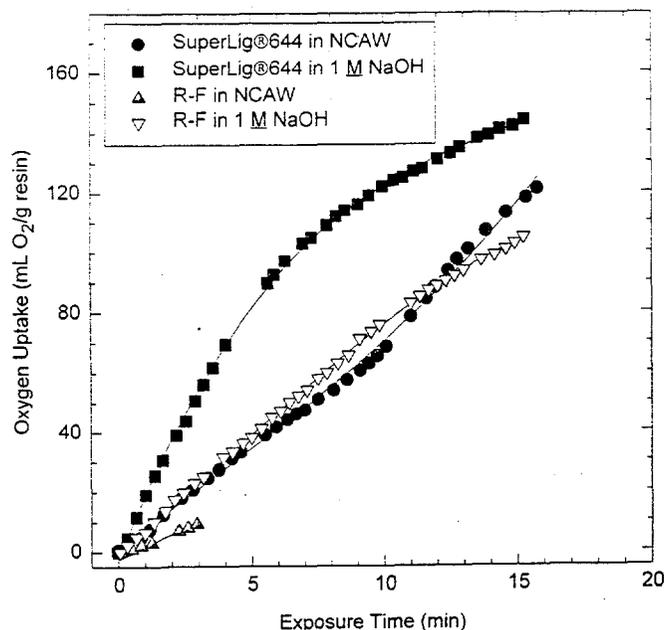


Figure 3.13. Oxygen Uptake of SuperLig®644 and R-F as a Function of Time in 1 M NaOH and NCAW Simulant Solution

It is interesting to note that the oxygen uptake is roughly linear for all solutions and materials tested except the SuperLig®644 in 1 M NaOH. Because the initial rate of O₂ uptake is much greater than others measured, it is possible that the oxygen supply available for resin degradation is limited by other factors. Because O₂ uptake by the resin is calculated by determining the volume change required to keep a constant pressure within a sealed system, it is possible that the O₂ concentration in solution might have decreased as it was consumed during the course of the experiment. If this were the case, the rate of uptake (slope of curve) would decrease, as is shown in Figure 3.13. Also, chemical changes to the resin during oxidation might hinder additional oxidation because all of the easily oxidized sites may have been removed.

An estimate of the average rate of O₂ uptake (Table 3.1) can be calculated from the slope of Figure 3.13. In addition, because the SuperLig®644 exhibits nonlinear behavior in 1 M NaOH, initial, final, and average rates are calculated. Assuming ideal gas law behavior and 100% O₂ at standard temperature and pressure (STP) (1 M O₂ at STP occupies 22.4 L), one can calculate an estimated oxygen uptake in mmol O₂ g⁻¹ h⁻¹. These calculations show that in a pure oxygen environment over the course of 16 h of exposure, SuperLig®644 exhibits a significant uptake of oxygen (0.78 mmol O₂ g⁻¹ h⁻¹) as compared to the overall capacity (3 mmol g⁻¹) of a standard ion exchange material.

Cesium Selectivity. After exposure of SuperLig®644 and R-F to oxygen, the samples were analyzed for cesium uptake by batch distribution (K_d) in an NCAW simulant solution. The solution had an initial Na/Cs mole ratio of 1.0E+04, and after contact the equilibrium Na/Cs was approximately

Table 3.1. Selected Oxygen Uptake Rates for SuperLig®644 and R-F in Various Solutions

Resin Material	Mass	Solution	Resin Oxygen Uptake	
			mL O ₂ g ⁻¹ h ⁻¹	mmol O ₂ g ⁻¹ h ⁻¹
SuperLig®644	0.82	1 M NaOH	1.74E+01	7.80E-01 ^(a)
SuperLig®644	0.82	1 M NaOH	4.10E+00	1.83E-01 ^(b)
SuperLig®644	0.82	1 M NaOH	9.30E+00	4.15E-01 ^(c)
SuperLig®644	0.54	NCAW	7.38E+00	3.29E-01
R-F	0.79	1 M NaOH	7.50E+00	3.35E-01
R-F	1.28	NCAW	3.22E+00	1.44E-01
(a) Initial rate averaged from 0 to 1.67 h.				
(b) Final rate averaged from 13.3 to 15 h.				
(c) Average rate from 0 to 15 h.				

1.0E+05. The K_d value measured for the SuperLig®644 decreased from approximately 1880 mL/g (no O₂ exposure) to 125 mL/g and 25 mL/g for 16-h O₂ exposure in NCAW and 1 M NaOH, respectively. These data have been converted from K_d to λ ($C_s K_d \times \rho = \lambda$) and are displayed in Figure 3.14 as a function of oxygen exposure. The λ value decreases nearly 40-fold in the NCAW solution. These results are to be expected based on the data displayed in Table 3.1; from these data it can be estimated that over the course of the 16-h exposure between 3 and 12 mmol O₂ are consumed per gram of SuperLig®644. This is roughly one to four times the number of stoichiometric sites on a typical ion exchange resin. Such massive oxygen exposures must undoubtedly change the structure of the organic polymer with potentially detrimental consequences to the exchange capacity.

Spectroscopic Analysis. In addition to O₂ uptake and cesium K_d measurements, the oxidized SuperLig®644 and R-F resins were analyzed by ¹³C NMR spectroscopy. The spectra for SuperLig®644 roughly illustrate the same patterns of oxidation noted in the previous sections. Because of the proprietary nature of the SuperLig®644 material, the NMR spectra cannot be reproduced in this report. However, general trends observed during the oxygen exposure experiments can be discussed. Two highly oxidized carbon functional groups were identified that were entirely absent from the unoxidized material. The magnitude of these signature peaks increased with exposure time from 0 to 16 h. In addition, these signature peaks are more prominent in the spectra of the samples exposed to oxygen in 1 M NaOH as opposed to the NCAW simulant. These results generally corroborate the batch K_d results from Figure 3.14. An additional peak was present in the unexposed resin, and the magnitude of this signal increases with O₂ exposure. This indicates that the SuperLig®644 material may be partially oxidized before initiation of the oxygen uptake experiments. Because no special storage conditions were specified by the manufacturer, the material was left in the dried "as received" form and kept under an air atmosphere.

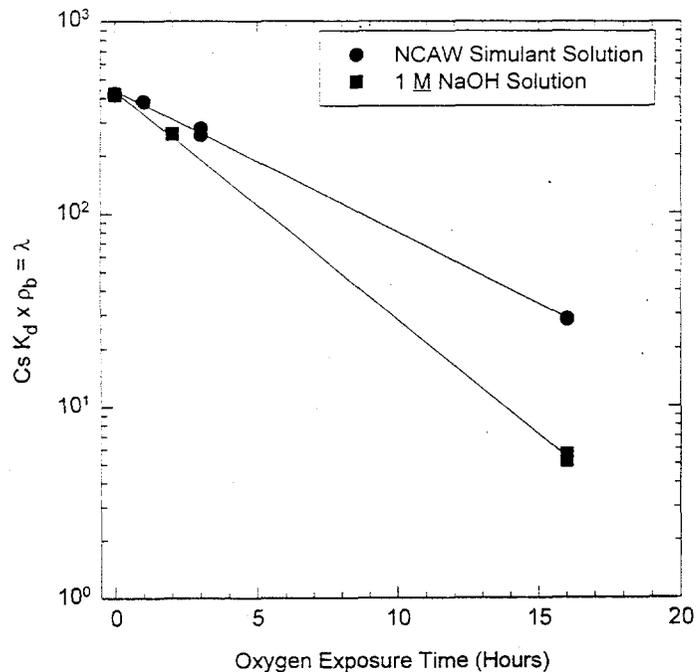


Figure 3.14. Cesium Loading of SuperLig[®]644 in Simulant NCAW Supernate (equilibrium Na/Cs = 1.0E+05) as a Function of Oxygen Exposure

Several peaks decrease during the oxidation process, which indicates that certain functional groups are affected by the oxidation process. In addition, several signals were completely removed by oxygen exposed in 1 M NaOH for 16 h. The spectra also indicate that certain functional groups are more susceptible to oxidation than others. It appears that these functional groups are readily susceptible to oxidation by oxygen dissolved in either 1 M NaOH or NCAW. Clearly, these spectra changes indicate extensive modification of the chemical structure of the SuperLig[®]644 resin during exposure to oxygen. However, these data also point to the utility of using NMR spectroscopy as a method of monitoring the chemical changes that may occur during oxidation and/or radiolysis of organic ion exchange materials.

Spectroscopic analysis of the R-F resin after exposure to oxygen in either 1 M NaOH or NCAW was also completed in a manner analogous to that of the SuperLig[®]644. The spectra also indicate susceptibility towards oxidation and structural modification by oxygen. However, the extent of R-F oxidation is not as great as the degradation observed for the SuperLig[®]644.

3.5.2 Radiation Stability

To evaluate the radiation stability of SuperLig[®]644, R-F, and CS-100, the materials were exposed to high-dose ⁶⁰Co gamma radiation within a sealed stainless steel reaction vessel. The sealed system allowed convenient measurement of gaseous decomposition products generated from solution and resin radiolysis. Gases released during the experiment were measured and identified by mass spectrometry.

In addition, the distribution coefficient (batch K_d) for ^{137}Cs uptake was determined and used an additional indicator of radiation damage to the resin material. The materials were exposed to a total radiation dose of approximately $1.0\text{E}+09$ rad at $1.6\text{E}+06$ rad/h over the course of several weeks.

The Gamma Irradiation Facility is operated by PNL and contains 37 stainless steel irradiation tubes positioned in a 7-ft-diameter by 13-ft-8-in.-deep stainless steel tank. Two arrays of ^{60}Co with a combined inventory of 32 kCi are located near the bottom of the tank. For radiation shielding, the tank is completely filled with water and a 3.5-ft-high concrete wall surrounds the top of the tank. The irradiation tubes, which are sealed on the bottom, vary in length and diameter from 16 to 18 ft and 1.8 to 6 in., respectively. The irradiation flux of the tubes range from 2×10^6 R/h to 2×10^2 R/h. The uniform flux region varies from ~6 in. for the tubes closest to the sources to greater than 12 in. for the tubes farthest from the sources. All flux measurements of the tubes are traceable to the National Institute for Standards and Technology.

All materials and test systems were lowered into the irradiation tubes manually and left in the tubes for the specific amount of time ($6.25\text{E}-01$, $6.25\text{E}+00$, $6.25\text{E}+01$, $6.25\text{E}+02$ h) to achieve the required exposure ($1.0\text{E}+06$, $1.0\text{E}+07$, $1.0\text{E}+08$, $1.0\text{E}+09$ rad). There is no activation associated with the gamma irradiation so the materials were transported to other facilities for cesium batch K_d evaluation after removal from the tubes. The temperature of the test was approximately 15°C to 20°C based on the recorded ambient temperatures in the gamma facility.

Approximately 25.6 g of NCAW simulant and 4.40 g of "as received" materials (e.g., R-F, CS-100, and SuperLig[®]644) were accurately weighed on an analytical balance (± 0.0001 g) and placed into separate 30-mL stainless steel irradiation chambers (1.6 cm i.d. x 15 cm). The limiting factor was the least dense material (SuperLig[®]644), because it is important that the total mass of material be constant for each irradiation. The total solution and resin volume could not exceed 25 mL to allow for resin expansion and expulsion of the generated gases during irradiation and gas sampling. The sample vessels were sealed with gas-tight fittings (copper metal knife edge vacuum flanges), pressure tested to 40 psi, and repeatedly evacuated and purged with high-purity argon to remove all residual gases. The vessels were removed from the radiation field and each gas sample was collected by purging the head-space above the resins into previously evacuated gas sampling devices. After the gas samples had been collected, ~0.1 g of material from each sample vessel was removed and stored in a refrigerated environment for later cesium batch K_d analysis. The sample vessels were resealed and purged repeatedly as previously described before additional radiation exposure. Gas samples were analyzed for CO_2 , CO , He , H_2 , N_2 , O_2 , N_2O , NO_x , NH_3 , CH_4 , C_2H_6 , and other hydrocarbons by mass spectrometry.

Gas Generation. Gases generated during static irradiation of the cesium-selective SuperLig[®]644, R-F, and CS-100 resins are displayed in Figures 3.15 through 3.17, respectively. The materials were irradiated at $1.6\text{E}+06$ rad/h. For all of the materials tested, hydrogen was the most abundant gas produced, followed by nitrogen, nitrous oxide, and oxygen. A small amount (less than 10% that of oxygen) of carbon monoxide was observed at high exposure. With the exception of oxygen, all of the gases evolved during the irradiation of SuperLig[®]644 exceeded those evolved from the R-F or CS-100 resins. The same trends are observed for the R-F resin with respect to CS-100. In general, it appears

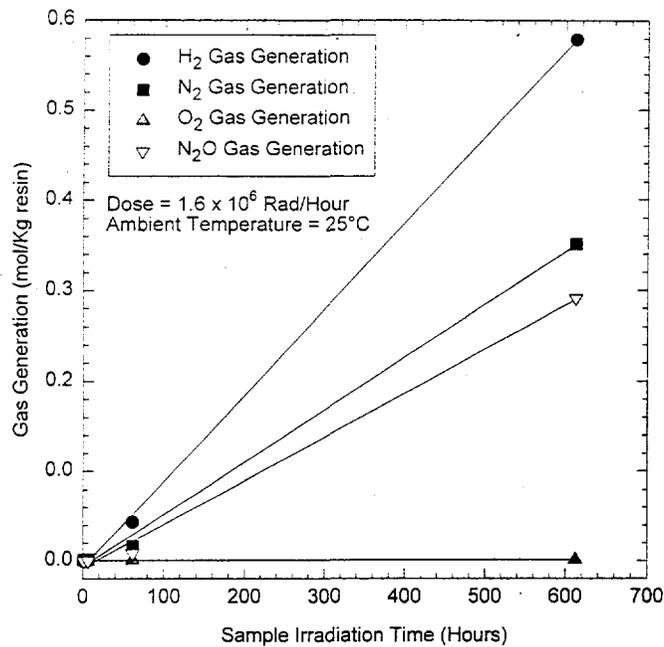


Figure 3.15. Gas Generation (mol/kg resin) During Irradiation of SuperLig[®]644 Exchanger in Simulated NCAW Supernate at 1.6E+06 rad/h

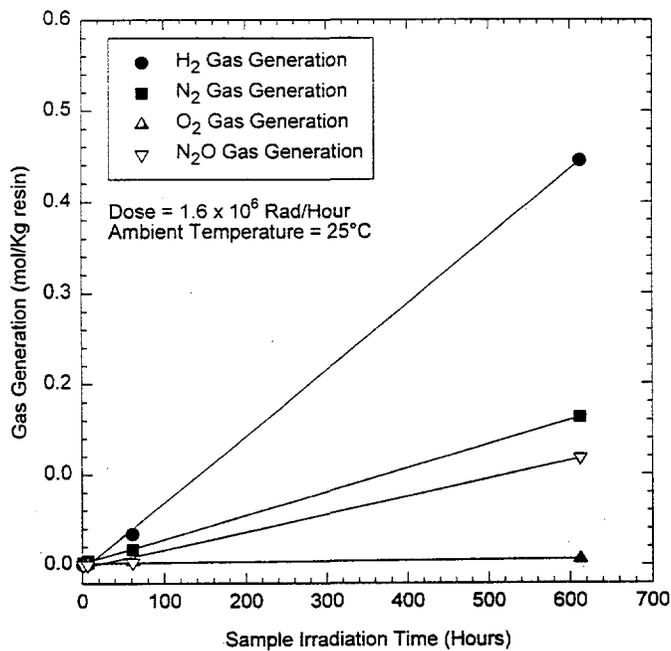


Figure 3.16. Gas Generation (mol/kg resin) During Irradiation of R-F Exchanger in Simulated NCAW Supernate at 1.6E+06 rad/h

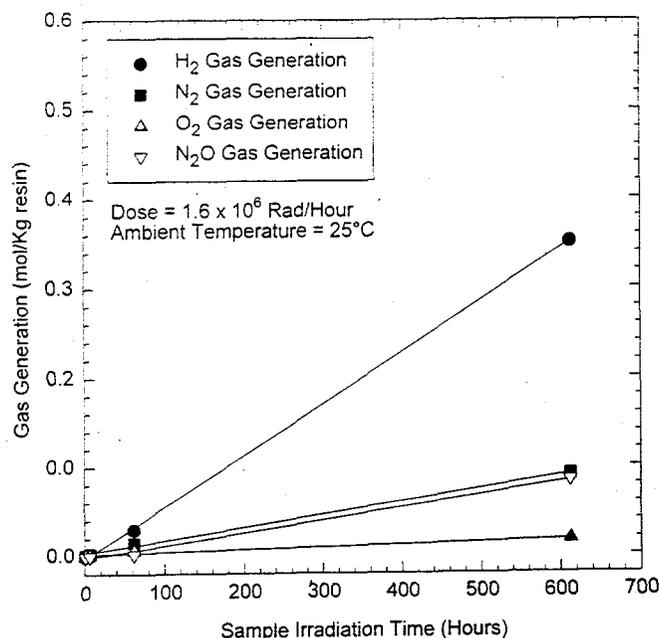


Figure 3.17. Gas Generation (mol/kg resin) During Irradiation of CS-100 Exchanger in Simulated NCAW Supernate at 1.6×10^6 rad/h

that gas generation increases in the following order: SuperLig[®]644 > R-F > CS-100. In contrast, evolution of oxygen follows the reverse order: CS-100 > R-F > SuperLig[®]644.

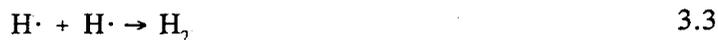
To reduce experimental costs, the normal background measurements were not collected. However, NCAW has been shown previously to evolve H₂, N₂, O₂, and N₂O during radiolysis (Bryan et al. 1993; Carlson et al. 1994). In addition, previous data also showed insignificant gas generation in the absence of radiation (0.0E+00 rad).

The gas generation G values are displayed in Table 3.2, where G is the number of molecules of each gas produced per 100 eV of energy absorbed. The values are useful for comparing the gas generation efficiency for each material. The trends observed in Figures 3.15 through 3.17 are readily apparent and quantified in Table 3.2. During radiolysis, the SuperLig[®]644 evolves 1.29 times the H₂, 1.56 times the N₂, 2.55 times the N₂O, but only 0.27 times the O₂ as compared to that given off by the R-F. When compared to CS-100, SuperLig[®]644 evolves 1.55 times the H₂, 2.17 times the N₂, 3.59 times the N₂O, and only 0.16 times the O₂. The apparent lack of oxygen evolution is unsurprising and was observed previously for the R-F resin (Bryan et al. 1993; Carlson et al. 1994). It can be explained in the following reaction sequence:

Table 3.2. G Values (molecules/100 eV) for Selected Organic Resins

Sample Material	Generation Efficiency				Dose Rate (rad/h)	Phase Ratio ^(a)
	G(H ₂)	G(N ₂)	G(O ₂)	G(N ₂ O)		
SuperLig®644	7.6E-02	3.9E-02	8.9E-04	2.8E-02	1.6E+06	5.82
R-F Resin	5.9E-02	2.5E-02	3.3E-03	1.1E-02	1.6E+06	5.82
CS-100 Resin	4.9E-02	1.8E-02	5.4E-03	7.8E-03	1.6E+06	5.82
NCAW Blank	1.6E-02	1.5E-03	7.5E-02	4.4E-05	1.5E+05	

(a) Liquid/solid phase ratio is the mass of NCAW solution divided by the mass of the organic resin (dry weight basis).



Hydrogen and oxygen are expected radiolytic products and result from the initial homolysis of the O-H bond of water initially forming H· and OH· radicals (Equation 3.1). The molecular decomposition products of pure water is a stoichiometric ratio of H₂ and O₂ (Equations 3.2 and 3.3). In the aqueous system containing either SuperLig®644, R-F, or CS-100, the radiolytic hydrogen to oxygen ratio is much higher than that for pure water because of the presence of a source of hydrocarbon material that is effective at scavenging OH· to reform water (Equation 3.4). This prevents hydroxyl radical recombination to form H₂O₂ and eventually the molecular decomposition product O₂. The H· radical can react with a like radical H· (Equation 3.3) or directly with the hydrocarbon resin to form H₂ (Equation 3.5). A reduced concentration of oxygen in the headspace above the resin during radiolysis indicates the relative stability of a material towards oxidation by dissolved oxygen. In this case, SuperLig®644 evolves less O₂ than either R-F or CS-100 and therefore must be more susceptible towards oxidation.

Nitrogen and nitrous oxide are both observed molecular decomposition products during the irradiation of SuperLig®644, R-F, and CS-100 in NCAW simulant solutions. These nitrogen-containing gases have been produced in similar systems containing nitrite and nitrate with organic carbon present (Bryan et al. 1992). Because the R-F and CS-100 resins do not contain organic nitrogen, the source of

nitrogen in N_2 and N_2O , must be from nitrate and nitrite in the NCAW simulant. Under reducing conditions in basic solution, nitrate and nitrite have been shown to be unstable toward reduction forming the gaseous products N_2 , N_2O , and NH_3 (Pourbaix 1974). Although ammonia has not been observed in this system, the organic is believed to be acting as the reducing agent toward nitrite and nitrate to form nitrogen and nitrous oxide. The chemical structure of SuperLig®644 is unknown, and N_2 or N_2O may originate from the above mechanism or the resin itself if organic nitrogen functional groups are present.

Cesium Selectivity. In addition to analysis of the gases evolved during radiolysis, the cesium selectivity of each material was determined as a function of radiation dose. A plot of the cesium λ value against total resin exposure in rads is shown in Figure 3.18. Duplicate measurements are displayed on the graph; therefore, the scatter in the data is thought to be significant. It is entirely possible that the chemical structure of the resin is changing continuously during radiolysis, thus affecting cesium selectivity. Free radicals may be formed within the polymeric structure and create different structures or cross-linking that may increase or decrease cesium selectivity and capacity. In previous experimental studies, lower K_d or λ values have been observed for several materials at a total dose of $1.0E+07$ rad (Bryan et al. 1993; Carlson et al. 1994). Before an increase back to the original unirradiated value at $1.0E+08$ rad, all materials exhibit a decrease in performance at the highest exposure dose.

After irradiation to $1.0E+09$ rad, the radiolysis experiment was terminated, and large amounts of resin materials were available for further testing. These materials were subjected to additional cesium batch K_d experiments at several different initial sodium/cesium ratios ($5.0E+02$, $5.0E+03$, $5.0E+04$, $5.0E+05$) to determine material cesium loading over a wide variety of cesium concentrations. The results are displayed in Figure 3.19 for SuperLig®644, R-F, and CS-100. At the Na/Cs mole ratio of the standard NCAW simulant ($1.0E+04$), the SuperLig®644 loading has decreased to approximately 41λ (λ approximates the number of column volumes required to reach 0.5 effluent (C)/inlet (Co) during column loading) while the R-F resin exhibits an estimated 120λ . Previous column loading experiments in NCAW (Brown et al. 1995) have indicated a loading of between 80 and 90 cv for unirradiated SuperLig®644. For R-F and CS-100 these values in NCAW have been estimated to be close to 190 and 35 cv (Kurath et al. 1994). From these data it appears that SuperLig®644 is the least stable material toward radiation exposure followed by R-F and CS-100. However, it should be noted that even after irradiation to $1.0E+09$ rad, the cesium loading of the SuperLig®644 and R-F resins is still greater than that of unirradiated CS-100.

3.6 Static Radiation of 3M Binders

Static radiation testing of a new proprietary 3M binder in distilled water continued during FY 1995. Similar material was previously irradiated in an NCAW simulant to ascertain chemical and radiation stability. The binder withstood a ^{60}Co gamma dose of 2×10^9 rad over a 6-week period with

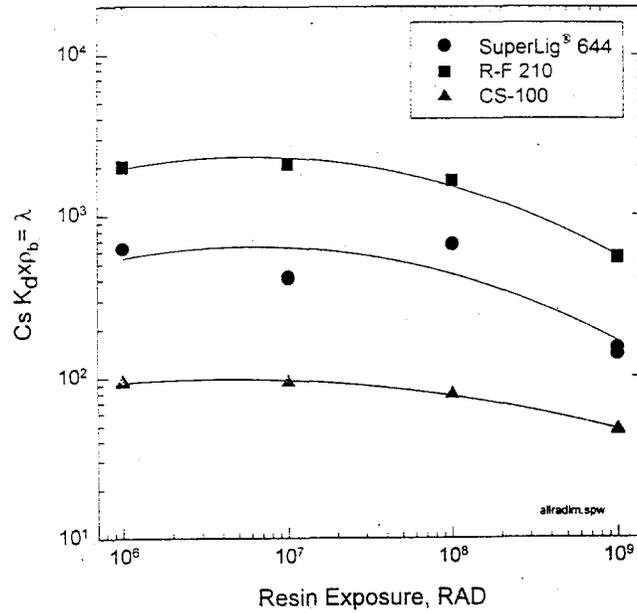


Figure 3.18. Cesium Selectivity of SuperLig®644, R-F, and CS-100 in Simulated NCAW Supernate (equilibrium Na/Cs = 1.0E+05) as a Function of Radiation Exposure

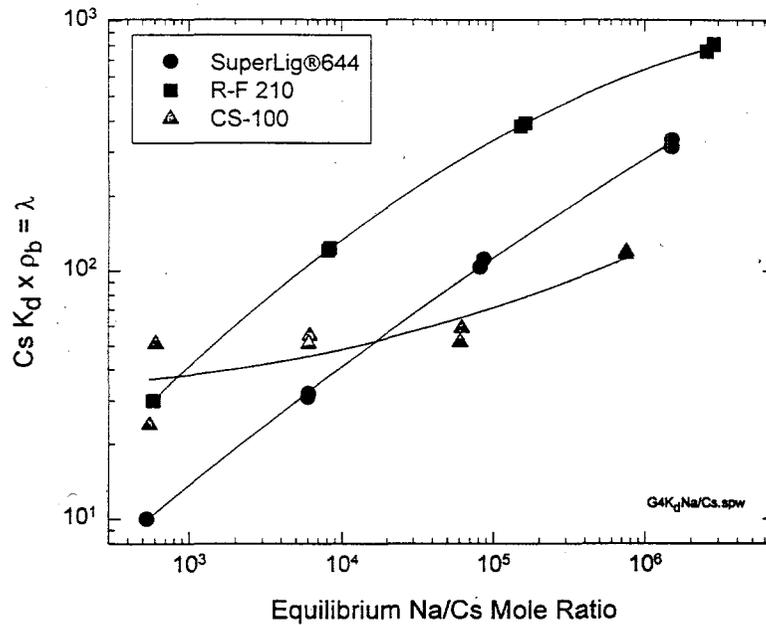


Figure 3.19. Cesium Selectivity of SuperLig®644, R-F, and CS-100 in Simulated NCAW Supernate (equilibrium Na/Cs = 5.0E+03 to 3.0E+06) After Total Exposure to 1.0E+09 rad

little or no visible damage. The material had been previously irradiated in an alkaline NCAW simulant to ascertain chemical and radiation stability. This is part of series of ongoing experiments and will be repeated on various binders and solutions as new materials become available.

3.7 West Valley O2 Facility

3M/PNL and West Valley (WV) staff continued the development of a test stand for ^{99}Tc removal from wastewater in the LLW O2 - WV treatment facility. The test equipment was delivered to WV. The equipment includes a pump, a prefilter, two 3M cartridges (each containing 1 ft² of active surface area) and a post filter. After several delays, the test stand was attached to the O2 Facility slip stream (0.1 gpm) on February 14 and tests were initiated. As anticipated by 3M, the prefilter plugged after 2 h and shut off the pump due to a high pressure drop. Additional pre-filters were installed. After 60 h the test was terminated because of high back pressure. The initial laboratory results show excellent chemical performance based on available ^{99}Tc detection limits. Selected samples were sent offsite to confirm the results. Additional tests are in progress after WV completes the change-out of two zeolite columns in the facility.

Initial results indicate that the ion exchange material successfully removed technetium. However, the experiment was prematurely terminated when the web loaded with solids. Additional tests centered around methods to reduce plugging by using alternate prefiltration techniques. A sample of WVNS water was sent to PNL. Testing showed that calcium and magnesium were present (hard water), and aluminum, consistent with zeolite fines and a carbon fluorine ratio (probably caused by the algae in the water), was also measured.

3.8 Special American Business Internship Training (SABIT) Program

V. M. Abashkin completed his internship at PNL under the Special American Business Internship Training (SABIT) program that was supported by ESP and the Department of Commerce. During his internship, Abashkin separated the cis-syn-cis and cis-anti-cis isomers of dicyclohexano-18-crown-6 (DCH-6) by using precipitation as the hydroxonium perchlorate complexes. The pure isomers were then subjected to gamma-radiation up to 1500 kGy. The starting materials and irradiated products were examined by infrared spectrophotometry and mass spectroscopy. The product distribution was analyzed in detail sufficient enough to propose a decomposition scheme for the two isomers.

As it turned out, the cis-syn-cis isomer was slightly more stable to gamma-radiation. In addition, dibenzo-18-crown-6 (DB-6) and the strontium complex of the cis-syn-cis isomer of DCH-6 were also irradiated. Quite unexpectedly, the only product isolated from irradiated DB-6 was DCH-6; i.e., the hydrogenation product. The strontium complex of DCH-6 was somewhat less stable than the free ligand.

3.9 Meetings and Site Visits

Interactions between WHC, INEL, WV, ORNL, and Westinghouse Savannah River Company (WSRC) continued to be strengthened during FY 1995. Site visits were completed at AS, WV, 3M, WSRC, ORNL, INEL, and IBC. A series of meetings were held at ORNL and Savannah River to transfer 3M/IBC/AS ion exchange technology. Staff from PNL and 3M reviewed the ESP program with members of each laboratory. M. C. Thompson of WSRC represented ESP at Savannah River while W. L. Kuhn, PNL, and J. S. Watson, ORNL, were in attendance at ORNL.

G. N. Brown presented a technical review of experimental work conducted under ESP to WHC personnel. The purpose of the meeting was to provide a quarterly update of experimental results for the Initial Pretreatment Module Project personnel.

L. A. Bray and G. N. Brown attended a videoconference of scientists from DOE-RL, PNL, WHC, and 3M. The purpose of the meeting was to initiate planning of a cesium removal demonstration using a large volume of actual waste to be obtained during the next 242-A Evaporator campaign at Hanford. SuperLig[®]644, R-F, CS-100 and crystalline silicotitanate were proposed as possible candidates for testing.

L. A. Bray, G. N. Brown, C. D. Carlson, and D. E. Kurath attended a meeting with personnel from PNL, WHC, SNL, and the Technical Advisory Panel to discuss the CS-100 and R-F cycle loading and elution testing and the actual waste batch testing of various ion exchange materials. Comments to the test plans were discussed and addressed.

4.0 Testing and Development of Novel Inorganic Ion Exchangers for Groundwater

(J. E. Amonette, H. T. Schaef, and X. Chen, PNL)

This section describes 1) testing of several newly developed inorganic ion-exchange materials for strontium and technetium under conditions typical of calcium-rich groundwater, alkaline high-level waste supernate, and a near-neutral low-level waste solution; 2) preliminary work towards development of tunnel-structure ion-exchange materials for both cationic and anionic contaminants; and 3) preliminary work towards development of a new process for separating radium from the ore material stored at Fernald, Ohio. The work described was performed during FY 1994 and FY 1995.

4.1 Testing of Strontium Exchangers in Calcium-Rich Groundwater

A preliminary assessment was made of the potential of several newly developed materials for the removal of aqueous strontium from groundwater by emplacement in subsurface permeable barriers. The key aspect being tested is the effect of competition from aqueous cesium typically present in groundwater at concentrations several orders of magnitude greater than aqueous strontium. The materials tested include a sodium titanate, three crystalline silicotitanates, one amorphous hydrous titanium oxide, a strontium-selective mica, two commercial zeolites, an R-F exchange resin and, for reference, one natural zeolite.

The ultimate goal of the work is to measure the equilibrium constant for strontium exchange by these materials in simulated Hanford groundwater. Consequently, the experimental design calls for approaching equilibrium from both supersaturation (i.e., adsorption) and undersaturation (i.e., desorption) with preliminary experiments to determine the kinetics of the reaction and to establish appropriate sample equilibration times. The kinetic data will also help in the assessment of the potential for use of these materials in permeable subsurface barriers. All experiments are conducted at 15°C to simulate actual groundwater temperatures at Hanford.

4.1.1 Experimental

Adsorbents Tested. A total of 11 specimens representing six distinct classes of materials are being tested (Table 4.1). Because of very limited quantities of the micas, the experimental design was constrained to use only 2 g of each material and one of the micas was only used for the equilibration portion of the study. Of the materials tested, only the zeolites and the R-F exchange resin were engineered forms. The remaining solids were tested as fine powders.

The solids were pretreated by three successive overnight washes (1:20 solid:solution) with a concentrated "groundwater" solution containing 40 μM Ca and 20 μM Na (i.e., ten times the

Table 4.1. Materials Class, Specimen Identification, and Sources of Novel Adsorbents Tested

Material Class	Specimen Identification	Source
Sodium titanate	Na-TIT	AlliedSignal Corporation, Des Plaines, IL (S.F. Yates, 708/391-3446) Texas A&M University College Station, TX (A. Clearfield, 409/845-2936)
Crystalline silicotitanate	DG-114 DG-120 NM DG-149 (CST)	Sandia National Laboratory Albuquerque, NM (J.E. Miller, 505/844-2565 (CST) or N.E. Brown, 505/845-8180) UOP Corporation Mt. Laurel, NJ (D. Fennelly, 609/727-9400) Texas A&M University College Station, TX (R.G. Anthony, 409/845-3370)
Hydrous titanium oxide	HTO	Sandia National Laboratories Albuquerque, NM (J.E. Miller, 505/844-2565 or N.E. Brown, 505/845-8180)
Zeolite	IE-96 TIE-9 ^(a) (IONSIV®)	Pacific Northwest Laboratory, Richland, WA (L.A. Bray, 509/376-0962) UOP Corporation Mt. Laurel, NJ (D. Fennelly, 609/727-9400)
	Clinoptilolite (CLINO)	Pacific Northwest Laboratory, Richland, WA (K.J. Cantrell, 509/376-8647) CH Deposit, Teague Minerals, Adrian, OR
Resorcinol-formaldehyde exchange resin	R-F	Pacific Northwest Laboratory, Richland, WA (L.A. Bray, 509/376-0962) Originally developed by J. Bibler, Savannah River Laboratory
Sodium brittle mica	MICA-1 MICA-BP	Pennsylvania State University University Park, PA (S. Komarneni, 814/865-1542)
(a) IE-96 zeolite coated with titanium oxide (Bray and Burger 1994)		

concentrations in the Hanford simulated groundwater used in the actual experiment). The solids were then washed with deionized water three times to remove excess salts, dried at 60°C overnight, and stored in a desiccator until use.

Simulated Hanford Groundwater. A stock solution of simulated Hanford groundwater (SHGW) was prepared that contained 4 mmol CaCl₂ and 2 mmol NaHCO₃ per liter. The initial pH of this solution was approximately 8.

Stock Strontium Solutions. A 1- μ M working solution of SrCl₂ was prepared in deionized water. Subsequent dilutions of this were made using SHGW for use in the study. The solutions were spiked with ⁸⁵Sr from SrCl₂ working solutions containing 300 - 500 μ Ci mL⁻¹.

Experimental Design. The overall experiment calls for equilibrium to be measured from both supersaturation and undersaturation. During the current term, only the supersaturation experiment was performed. Details of the undersaturation experiment are given for reference purposes, however.

Approach from Supersaturation. For each material, the equilibrium measurements from supersaturated conditions involved duplicate measurements at each of five starting strontium concentrations (100 μ M, 10 μ M, 1 μ M, 100 nM, and 10 nM) after the appropriate equilibration time. The first set of preliminary kinetic experiments used two concentrations only. However, at the end of this period, equilibrium had not been reached and a second set of kinetic experiments were set up to run for longer incubation periods (9, 29, 50, 76, and 96 days). A third set of samples for the equilibrium determinations were set up at shortly after the start of the second kinetic study and were sampled after 127 days. A series of blanks containing the solutions but no solid phases were carried through both the kinetic and equilibrium portions of the experiment. The original design is shown below:

	<u>t1</u>	<u>t2</u>	<u>t3</u>	<u>t4</u>	<u>t5</u>	<u>teq</u>
C1	1	1	1	1	1	2
C2						2
C3						2
C4						2
C5	1	1	1	1	1	2

In the original design, each material required 10 tubes for the kinetic experiment and 10 tubes for the equilibrium experiment. The total number of vials was 220 for ten materials and one blank. However, with the addition of the second kinetic experiment, the total number of tubes required rose to 330.

Approach from Undersaturation. Equilibrium measurements from undersaturated conditions will involve an initial loading of strontium onto duplicate samples of each material using the five starting strontium concentrations and appropriate equilibration time established in the supersaturated experiment followed by replacement of the equilibrium solution with a fresh solution of simulated groundwater

containing no strontium. We plan to use the solids equilibrated in the supersaturation experiment after they have been counted. The undersaturated samples will be measured after sufficient time has elapsed for the new equilibrium to be established. As in the supersaturation experiment, preliminary kinetic experiments used to determine the appropriate desorption equilibration time will involve single measurements after each of five incubation periods for the highest and lowest starting strontium concentrations only. The undersaturated experiments, therefore, will also involve ten tubes each for the kinetic and equilibrium portions (20 tubes per material or blank, 220 tubes for the undersaturation portion of the experiment).

Procedure. Batch adsorption experiments were conducted in 4-mL plastic gamma-counting tubes using a solid:solution ratio of 1:20. Each tube contained 100 mg of sample and 2 mL of the appropriate SrCl₂ solution in SHGW that had been spiked with approximately 2 μCi (~0.5 pmols) of ⁸⁵Sr. The solutions were pre-chilled to 15°C before addition to the samples, and the mixtures were incubated at the same temperature in a shaking water bath. At the end of each incubation period, the samples were removed from the water bath and centrifuged to a clear supernatant. Exactly 1.000 mL of supernatant was then collected and transferred to a second gamma tube. Both the original tube (containing the solid phase and 1 mL of supernatant) and the second tube (containing 1 mL of supernatant only) were then counted for ⁸⁵Sr activity. Distribution coefficients for strontium [$K_d(\text{Sr})$, mL g⁻¹] on the solid phase at each sampling time were then calculated from the background-corrected counts for the original tube minus the background-corrected counts for the 1 mL of supernatant and normalized to 1 g of solid, all divided by the background-corrected counts for the 1 mL of supernatant; i.e.,

$$K_d(\text{Sr}) = (C_{\text{solid}} - C_{\text{super}})/(W_{\text{samp}} * C_{\text{super}}) \quad 4.1$$

where C_{solid} and C_{super} refer to background-corrected counts for the first and second gamma tubes, respectively, and W_{samp} to the oven-dry weight of solid in the tube. The K_d values are conservative in that any solid that might have been included in the supernatant count (several of the materials were fine powders) would tend to lower the K_d .

4.1.2 Results and Discussion

The kinetics of adsorption were much slower than originally thought, and as a result, much longer equilibration times and a second set of samples were needed to come close to equilibrium.

The materials exhibited three distinct kinetic patterns during the adsorption experiment. The most common pattern is shown by the sodium titanate (Na-TIT), for which no difference in the K_d s for the 10 nM and 100 μM strontium solutions were identified and equilibrium had essentially been reached after 76 days of incubation (Figure 4.1a). The R-F exchange resin exhibited the same type of pattern except that the K_d s for the 10 nM and 100 nM strontium solutions were different by a factor of 40 (Figure 4.1b). This difference probably stems either from a very limited number of strontium-selective exchange sites on the resin relative to the amount of strontium in solution, or to a distribution of sites having different strontium selectivities on the resin. Thus, the highly selective sites on the resin are

saturated with strontium at the 100- μM level and the K_d is significantly lower. A slight "saturation" effect was also seen for the hydrous titanium oxide (HTO) and DG-120 CST samples and would be expected in poorly crystalline materials having a variety of exchange sites.

The Na4 mica sample was unique among the materials tested in that it required the entire 96 days incubation period to reach equilibrium (Figure 4.1c). The K_d for this material increased by an order of magnitude between the 9 days and 96 days samplings. The time-dependence of the $K_d(\text{Sr})$ for this material could be fit to a power law expression for periods of 1 day and longer (Figure 4.1d).

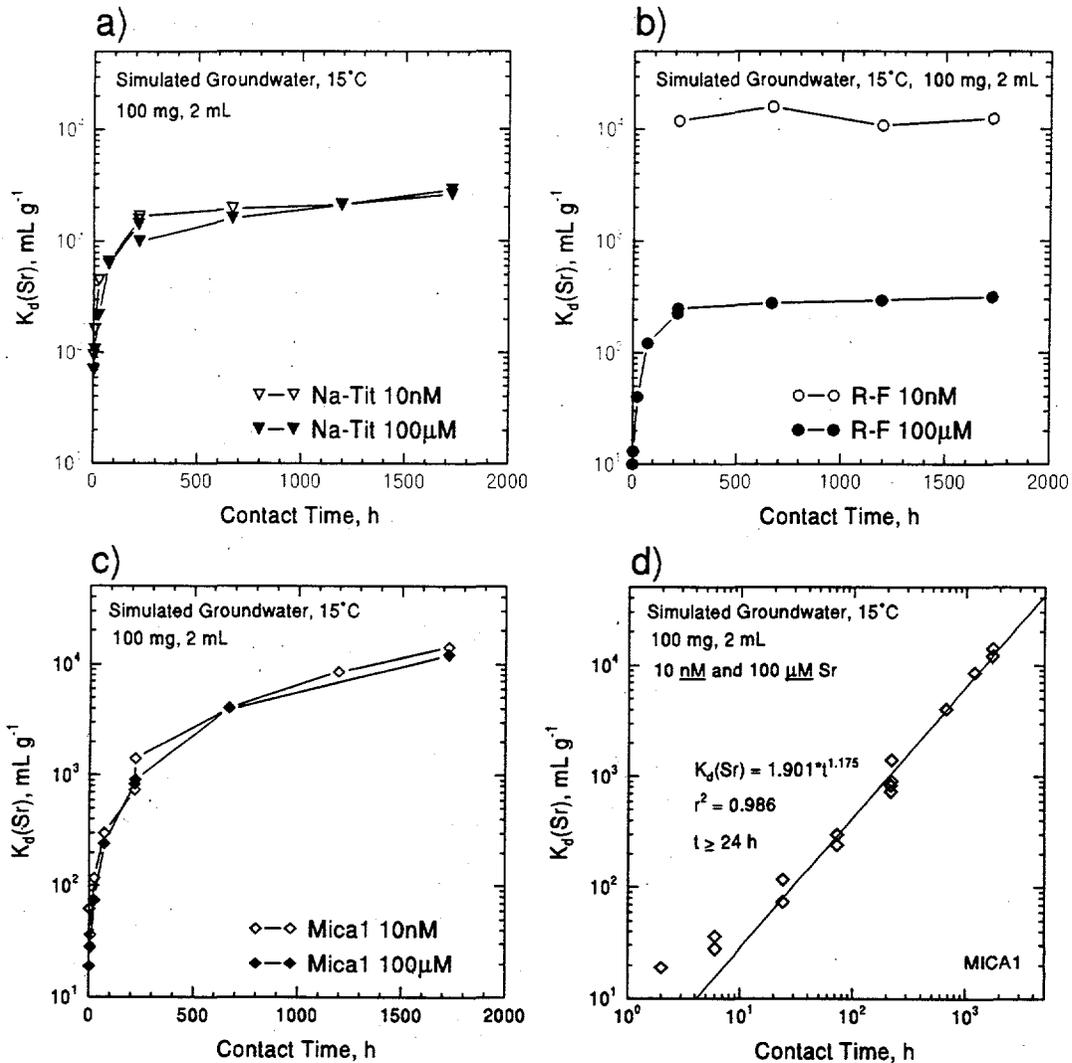


Figure 4.1. Changes in the Distribution Coefficient with Incubation Time for Strontium Removal from Simulated Hanford Groundwater (4 μM CaCl_2 and 2 μM NaHCO_3) at 15°C by a) sodium titanate, b) an R-F resin, c) mica, and d) same as c) showing power law fit to data

Extrapolation of the expression suggests that a strontium K_d of 10^5 would eventually be reached in about 16 months. Similar power-law kinetics have been reported for release of potassium from lower-charged micas (Havlin et al. 1985) and presumably stem from the slow ion-diffusion processes occurring in the interlayer region of the mica in response to the concentration gradient imposed by the bulk solution. The mica also is believed to have a different alignment of the layers when saturated with monovalent ions such as sodium than when it is saturated with hydrated divalent ions such as magnesium and calcium. This alignment would be expected to impose a significant activation energy barrier to the adsorption of strontium and may be responsible for the slow kinetics observed. Even though the mica was treated with concentrated calcium-rich groundwater for three nights, it has become evident from subsequent experiments that little of the sodium was replaced by this treatment. We now know how to prepare a completely magnesium-saturated form of the mica that, presumably, would have a lower energy barrier to strontium exchange and faster kinetics. This will be tested in FY 1995.

The zeolites achieved equilibrium in a matter of a few weeks and showed essentially no difference in their final K_d values (Figure 4.2). The HTO and CST samples were clearly the most selective adsorbents for strontium (Figure 4.3), yielding K_d s from 104 to as high as 10^6 mL g^{-1} . The HTO sample reached equilibrium relatively quickly, as did the DG-114 CST (Figure 4.3a and 4.3b). The DG-120 sample, on the other hand, reached a maximum K_d after 50 days and then the K_d decreased by the time of the 76-day sampling (Figure 4.3c). Even so, the maximum K_d s measured for this sample were very large, ranging from 2×10^5 to nearly 10^6 mL g^{-1} . This sample showed some evidence of the "saturation" behavior noted earlier for the R-F resin, which is probably due to a greater heterogeneity of sites and a lower crystallinity (confirmed by X-ray diffraction) than seen with the other two CSTs. The DG-149 CST sample yielded K_d s near 10^5 mL g^{-1} , but it is not clear whether equilibrium was reached. The measurement of such high K_d s is subject to some analytical error in the solution phase measurement due to very low ^{85}Sr count rates, but the duplication for readings obtained at different concentrations suggests that the time-dependent pattern of the K_d data for this sample is not random.

The kinetic data for all the specimens are summarized by strontium concentration in Figure 4.4. The time scale is expanded to focus on the first 3 days of incubation in Figures 4.4a and 4.4c. Clearly, during this time period, the CST samples and the HTO sample are one to two orders of magnitude more selective for strontium than the other adsorbents. In the long term, CSTs maintain their selectivity by at least an order of magnitude the other adsorbents, but there is a close race for second place between the mica, the HTO and, at low strontium concentration, the R-F resin (Figures 4.4b and 4.4d).

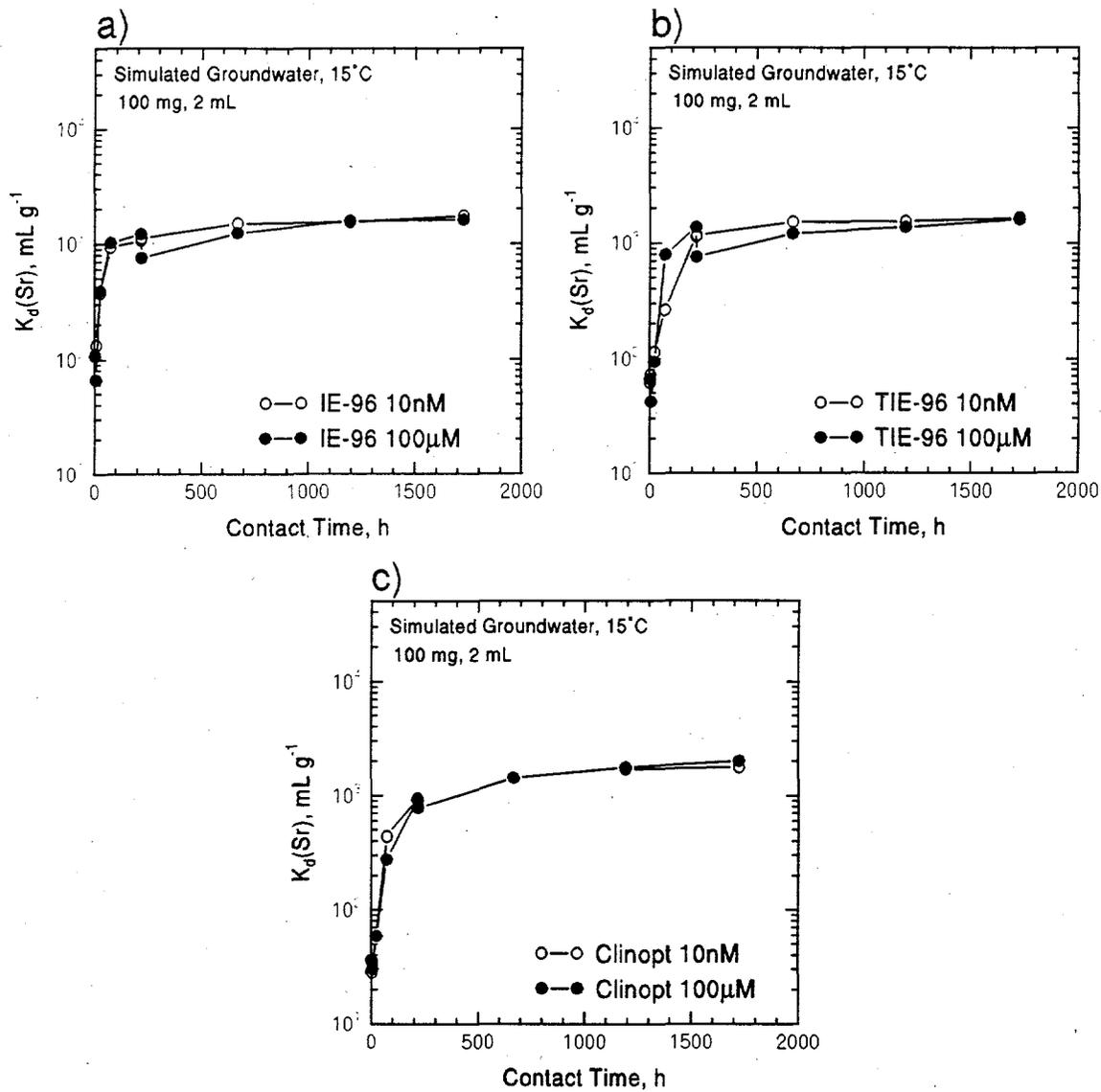


Figure 4.2. Changes in the Distribution Coefficient with Incubation Time for Strontium Removal from Simulated Hanford Groundwater ($4 \mu\text{M}$ CaCl_2 and $2 \mu\text{M}$ NaHCO_3) at 15°C by Three Zeolites: a) IE-96, b) TIE-96 (a titanium-oxide coated version of IE-96), and c) natural clinoptilolite

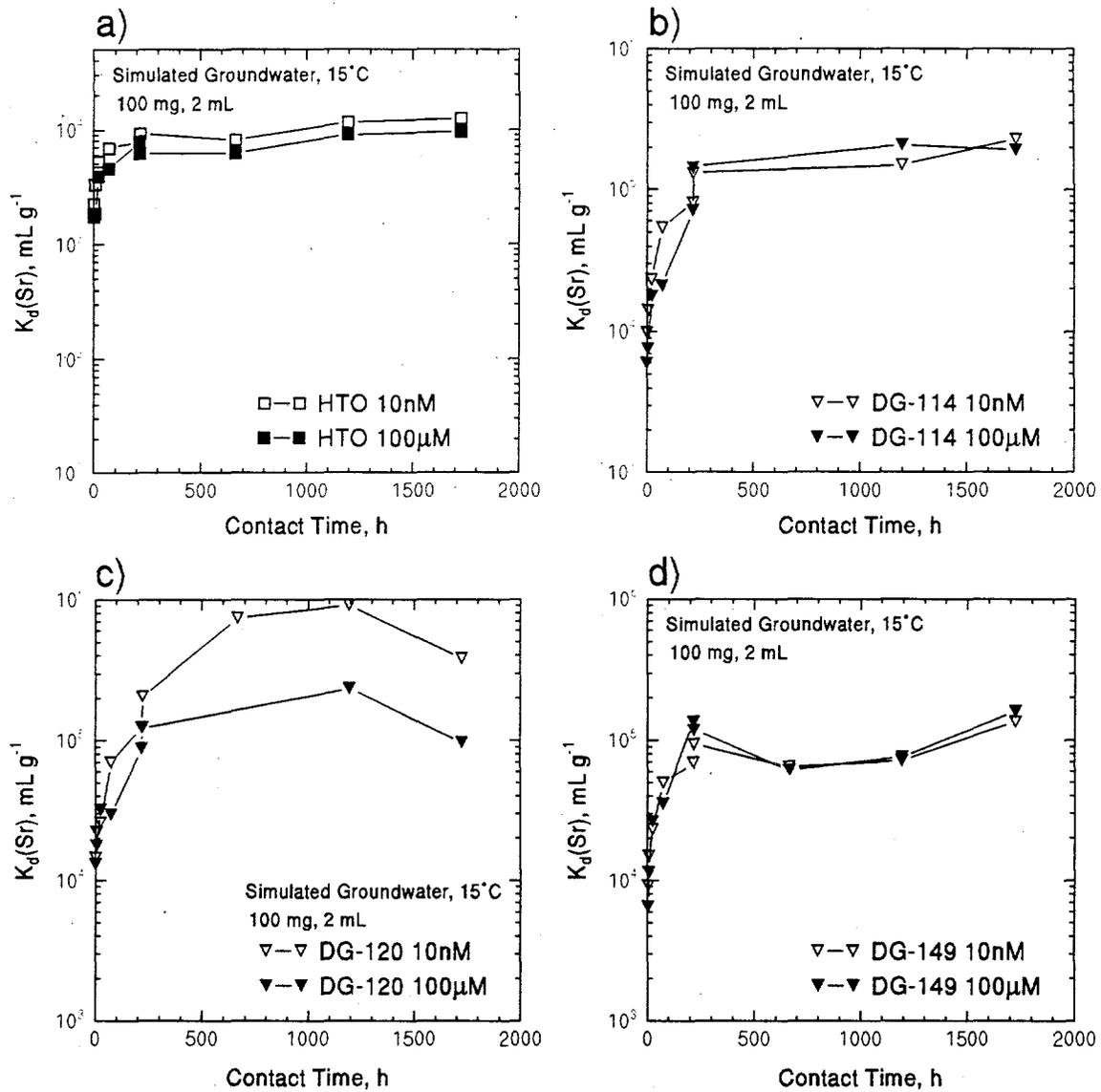


Figure 4.3. Changes in the Distribution Coefficient with Incubation Time for Strontium Removal from Simulated Hanford Groundwater ($4 \mu\text{M}$ CaCl_2 and $2 \mu\text{M}$ NaHCO_3) at 15°C by a) hydrous titanium oxide and three crystalline silicotitanates: b) DG-114, c) DG-120, and d) DG-149

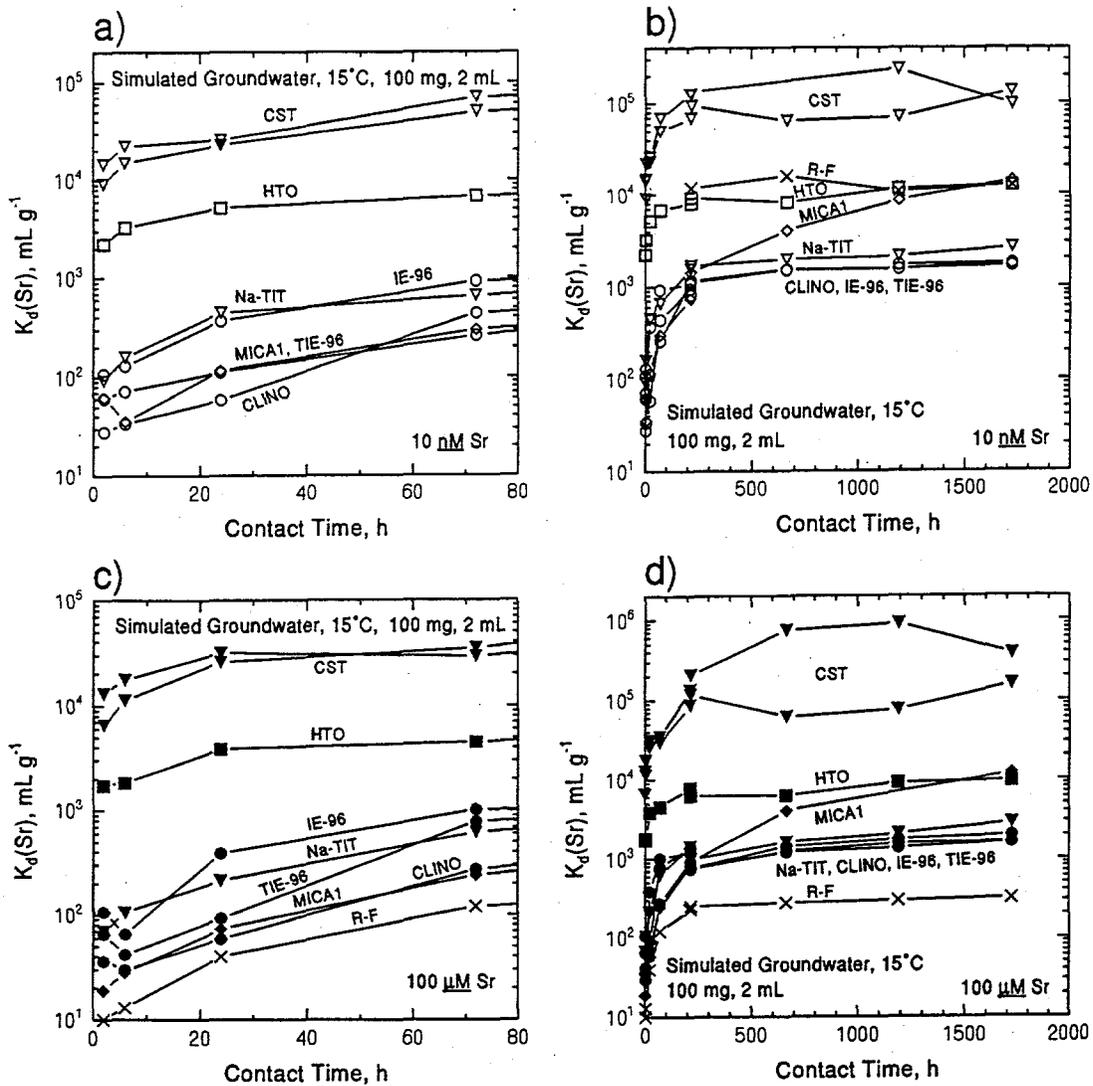


Figure 4.4. Changes in the Distribution Coefficient with Incubation Time for Strontium Removal from Simulated Hanford Groundwater ($4 \mu\text{M CaCl}_2$ and $2 \mu\text{M NaHCO}_3$) at 15°C by Ten Novel Adsorbents: a) and b) 10 nM strontium initial concentration, c) and d) $100 \mu\text{M}$ strontium initial concentration

The results of the equilibrium experiment showed essentially no change in K_d with initial concentration of strontium (Figure 4.5), suggesting that none of the absorbers was near to saturation with strontium. Indeed, calculations of the fraction of the exchange sites occupied by strontium indicated that, at most, about 0.2% of the exchange capacity was consumed by strontium adsorption. Thus, the "saturation" effects seen in a few samples (e.g., R-F, DG-120) during the kinetic study were not seen in the equilibrium study. We have no explanation for this difference, other than to note that long equilibration times with continuous shaking may have resulted in particle abrasion and the creation of new exchange sites that would eliminate the original "saturation" effect. In future experiments, this possible artifact can be avoided by shaking the samples periodically rather than continuously.

A comparison of the K_d s obtained in the 127-day equilibrium study with those after 96 days of contact in the kinetic study (Figure 4.6) showed reasonable agreement. For all absorbers, higher K_d s were obtained for the 127-day equilibration, but in some instances (e.g., IE-96, MICA1, Na-TIT, and HTO) these values were substantially greater than those obtained with the 96-day equilibration. Both data sets, however, show the CST and HTO samples to have the highest and the zeolites (CLINO, TIE-96, and IE-96) the lowest K_d s.

It is tempting to confuse the K_d s reported here with rational selectivity coefficients. In fact, the K_d values are estimates of selectivity per unit mass of adsorbent and, due to differences in particle size, density, exchange capacity, etc., are at best only rough indicators of site-specific selectivity. For comparisons among different materials, therefore, a better estimate of inherent site-specific selectivity would involve conversion of the mass-based K_d values to numbers based on exchange capacity. That is,

$$K_d EC \text{ (mL/meq)} = K_d \text{ (mL/g)} / \text{Exchange Capacity (meq/g)}. \quad (4.2)$$

Unfortunately, the proprietary nature of several of the adsorbents did not allow us to make exchange capacity measurements for calculation of site-specific K_d s. An example of a situation where mass-based K_d s are misleading is given in Section 4.2.

4.2 Testing of Strontium Exchangers in Alkaline High-Level Waste Simulant

Two sodium nonatitanate samples (from AS) and a monosodium titanate sample (from Boulder Scientific) were tested for strontium removal from a high-pH aqueous simulant typical of tank waste at the Savannah River Site. The nonatitanate samples tested were of the newly developed engineered form in two particle sizes: 1) a <40-mesh sample, and 2) this sample wet-ground to produce a slurry of particles on the order of a few microns in diameter. The monosodium titanate was tested as received; i.e., a slurry of particles ranging in diameter from 1 to 36 μm . Tests were performed in triplicate using the Strontium Decontamination Test Procedure, Revision 2, dated 10 July 1991, from the Savannah River Testing Center (specification Z-SPP-H-00001), supplied by M. C. Thompson.

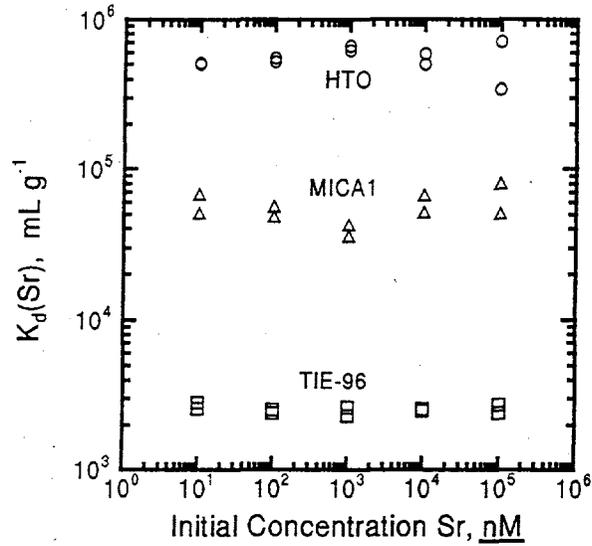


Figure 4.5. Effect of Initial Strontium Concentration on Equilibrium Values of the Distribution Coefficient for Strontium Removal from Simulated Hanford Groundwater ($4 \mu\text{M}$ CaCl_2 and $2 \mu\text{M}$ NaHCO_3) at 15°C by Three Novel Adsorbents

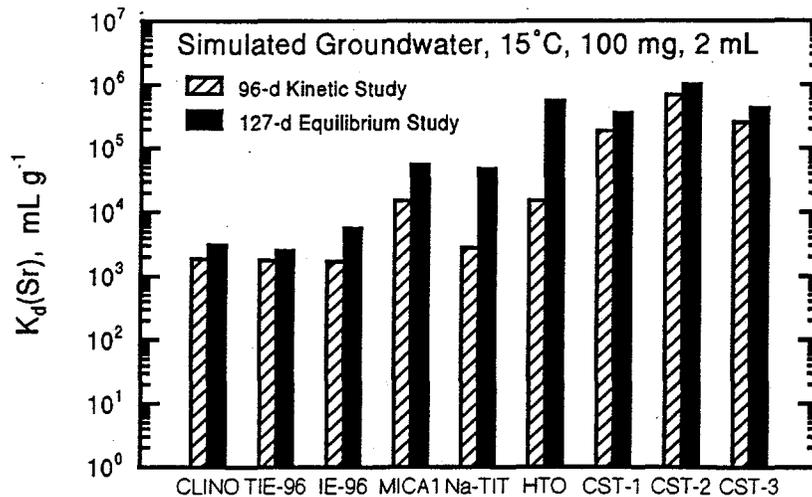


Figure 4.6. Comparison of the 127-day Strontium Distribution Coefficients for Ten Novel Adsorbents from the Equilibrium Experiment with Those Obtained After 96 Days in the Kinetic Experiment

The results (Figure 4.7) showed 48-h K_d s of 45,000 mL g⁻¹ for the <40-mesh nonatitanate, 270,000 mL g⁻¹ for the same material ground to a fine slurry, and 240,000 mL g⁻¹ for the monosodium titanate 1- to 36- μ m slurry. These results clearly show the impact that surface area has on the measured K_d s (as discussed in Section 4.1), and demonstrate that the engineered form of the AS nonatitanate should be able to equal or better the performance of the Boulder Scientific monosodium titanate materials currently used at SRTC.

4.3 Testing of Technetium Exchangers in Low-Level Waste Simulant

This test was designed to assess the ability of several novel exchangers prepared at PNL to remove TcO_4^- at very low levels from groundwater. The specific site for application of this information was the low-level waste treatment facility (02 facility) at West Valley Nuclear Services (WVNS) in upstate New York. Levels of ^{99}Tc there are about 7.5 nCi L⁻¹ (16 dpm mL⁻¹, 4.5 nM). The site operators wished to see a decontamination factor ($\text{DF} = \text{Conc}_{\text{out}}/\text{Conc}_{\text{in}}$) of 100 using a water discharge rate of 40 gpm. Initial batch tests at WVNS with one of the novel exchangers (Aliquat-treated A-51) lowered the ^{99}Tc levels to below the detection limit of 0.13 nCi mL⁻¹. However, using this limit in calculations yielded a K_d of >1800 mL g⁻¹ at a 33:1 solution:solid ratio and a corresponding DF of >58. Under the conditions of the earlier test, a K_d of 3300 mL g⁻¹ was needed to yield a DF of 100. In the current test, therefore, we used a higher solution:solid ratio in an attempt to avoid detection-limit problems and determine whether the novel exchangers could meet the DF criteria set by the WVNS facility operators.

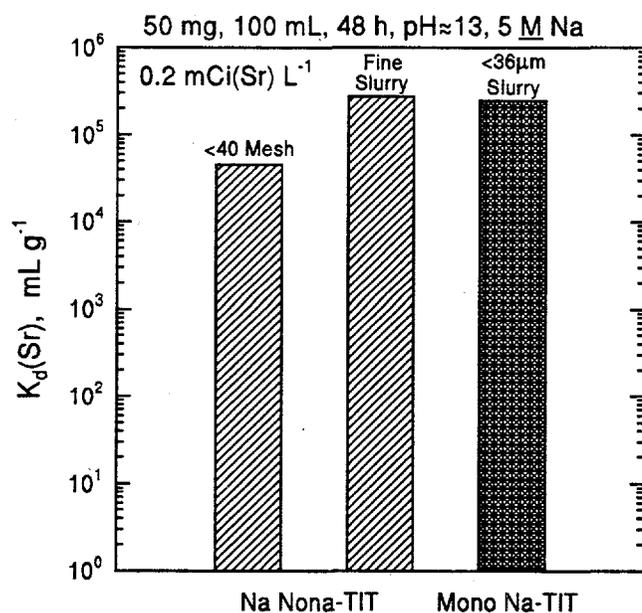


Figure 4.7. Comparison of the Strontium Distribution Coefficients Obtained for Sodium Nontitanate and Monosodium Titanate Ion Exchangers Using the SRTC Procedure. Note the effect of particle size on the nonatitanate K_d s.

4.3.1 Experimental

Experimental Design. Seven novel exchangers were tested, consisting of SiO₂ and ZrO₂ supports treated with solutions containing 1, 5, and 10 wt% Aliquat™ 336 (methyltricaprylammonium chloride), and zeolite IONSIV®A-51 treated with a 10 wt% Aliquat™ 336 solution. The tests involved two solution:solid ratios (2000:1 and 1000:1) and synthetic groundwater at two pH levels (7 and 10), and were performed in triplicate.

Materials. Experiments were conducted in 50-mL conical-bottomed centrifuge tubes using 25- or 50-mg exchanger samples and 50 mL of simulated groundwater solution. Two batches (pH 7 and 10) of synthetic groundwater (5 μM CaCl₂ and NaHCO₃, pH adjusted with NaOH) were prepared immediately before use. The groundwater was spiked with ⁹⁹Tc to a level of 7.5 nCi L⁻¹ and stored in a tightly capped container to minimize CO₂ exchange and technetium volatilization.

Testing Procedure. The exact amounts of simulated groundwater added to each tube were determined gravimetrically. The tubes were tightly capped and equilibrated in a shaking water bath at room temperature. After 48 h, the tubes were removed, centrifuged to a clear supernatant, and about 20 mL of this solution transferred by pipet into a scintillation vial. From this vial, 4 mL of solution were transferred into a second scintillation vial containing 16 mL of scintillation cocktail and then the beta activity determined. With each run, three samples of the appropriate unspiked groundwater solution (4 mL in 16 mL of cocktail) were also counted as an estimate of background.

Calculations. The K_d and DF values were calculated as follows:

$$K_d = \frac{(\hat{C}_{\text{blank}} - C_{\text{samp}} - 2\hat{C}_{\text{bkgrd}})(V_{\text{scint}})}{(C_{\text{samp}} - \hat{C}_{\text{bkgrd}})(WT_{\text{samp}})(V_{\text{samp}})} \quad (4.3)$$

$$DF = (\hat{C}_{\text{blank}} - \hat{C}_{\text{bkgrd}}) / (C_{\text{samp}} - \hat{C}_{\text{bkgrd}})$$

where \hat{C}_{blank} is the average raw counts obtained for the three spiked samples that did not contain exchanger, C_{samp} is the raw counts obtained for the sample, \hat{C}_{bkgrd} is the average raw counts obtained for the three unspiked groundwater samples, and WT_{samp} is the weight of the sample in grams.

4.3.2 Results and Discussion

Because of the very low activity of ⁹⁹Tc in solution, significant adsorption from solution yielded supernate activities very close to background levels. Thus, the 50-mg samples had very low supernate activities and data were not considered reliable. The results for the 25-mg samples (Figure 4.8) showed higher K_ds for greater loading of Aliquat™ 336 on the solid supports. Adsorption was greater at pH 7 than at pH 10, most likely due to lower ionic strength in solution and higher net positive surface charge at pH 7 than at pH 10.

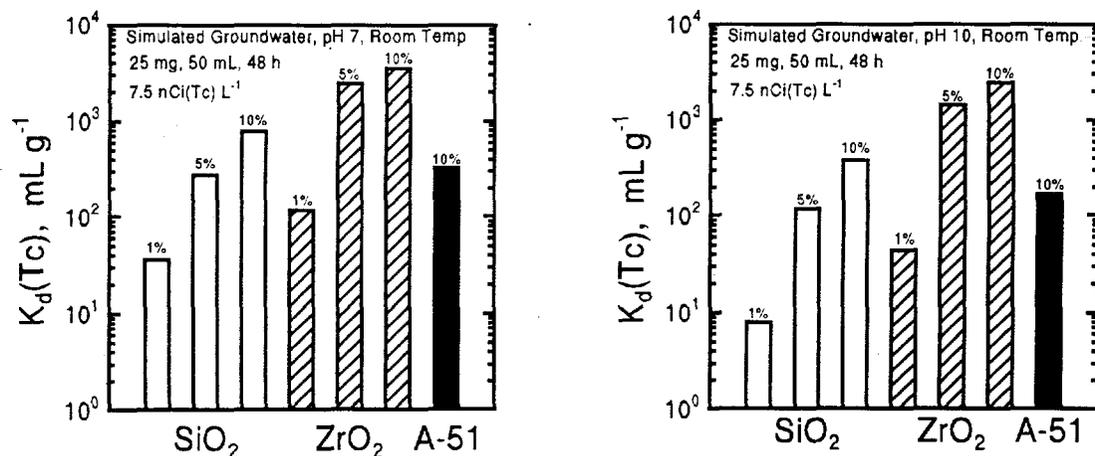


Figure 4.8. Values of Technetium Distribution Coefficients (48 h) in Simulated Groundwater at pH 7 and 10 Obtained with Three Support Materials Prepared by Treatment with 1, 5, and 10% Aliquat™ 336 Solutions

Of the three supports, the ZrO₂ yielded the highest K_ds per unit of Aliquat™ 336. The ZrO₂ support treated with the 10% Aliquat solution yielded K_ds of about 3500 mL g⁻¹ at pH 7 and 2400 mL g⁻¹ at pH 10. This ion exchanger, therefore, met the criteria of 3300 mL g⁻¹ at pH 7 and was very close to meeting the criteria at pH 10.

4.4 Development of Inorganic Tunnel-Structure Ion Exchangers

In FY 1995, preliminary studies began that were aimed at identifying, synthesizing, and testing new types of inorganic ion exchangers based on the minerals having tunnel-like structures. The advantages of the inorganic ion exchangers are that they are generally more stable to radiation than organic resins and often can be used as both separation agent and waste form, thus eliminating an extra step in the waste processing. The tunnel-structure materials offer three-dimensional sites for retention of ions similar to the zeolites or the layered exchangers such as micas and titanates. A classic example of a tunnel-structure exchange material is CST, which has an internal tunnel cavity with extremely high selectivity for cesium and apparently for strontium as well (as shown in Section 4.1).

The tunnel-structure compounds can serve as either anion or cation exchangers depending on the degree of hydroxylation of the inner surfaces of the tunnel. Natural examples of tunnel-structure cation exchangers are hollandite (barium form) or cryptomelane (potassium form), manganese(IV) oxides belonging to the todorokite family (Turner and Buseck 1981) and having little or no hydroxylation (Byström and Byström 1950). The analogous anion exchanger is akaganeite (MacKay 1962), an iron(III) oxyhydroxide, which forms with chloride as its counter ion and contains numerous hydroxyl groups. Recently, schwertmannite, a mineral with the akaganeite structure but with sulfate as the

counter ion, was reported (Bigham et al. 1994). A schematic of an akaganeite-structure compound having a tetrahedral anion such as SO_4^{2-} or TcO_4^- as the counter ion is shown in Figure 4.9.

Our interest in the tunnel-structure compounds began with the recognition that the $\alpha\text{-MnO}_2$ todorokite-type minerals have strong affinities for large monovalent and divalent cations such as potassium, rubidium, and barium (Tsuji and Abe 1984) when the size of the tunnel is two octahedra on a side (i.e., 2×2). Presumably, they would have even higher selectivities for radium, based on measured selectivities for potassium and rubidium, ions that are similar in ionic radius to barium and radium, respectively. Other layered manganese oxide compounds have also been shown to have very high selectivities for lithium and are useful for the recovery of this element from seawater and brine solutions (Miyai et al. 1988; Ooi et al. 1987; Sagara et al. 1989; Tsuji et al. 1992).

The hydroxylated tunnel-structure compounds attracted interest for their ability to retain anions. In addition to charge, anion exchangers are also sensitive to the shape of the anion for determining their selectivity. An example of this is the higher selectivity of hydrotalcite-like minerals for the carbonate ion relative to the sulfate ion (Miyata 1983), largely as a result of anion shape (trigonal planar vs. tetrahedral). In looking for a possible inorganic anion exchanger for TcO_4^- , we determined that a layered compound such as hydrotalcite would probably have a low selectivity, but that a tunnel-structure material would tend to favor tetrahedral anions such as TcO_4^- and CrO_4^{2-} over the trigonal planar anions such as carbonate and nitrate and thus would be suitable for groundwater applications. The additional stability of the layered exchangers for planar ions is largely a result of the variable spacing of the layers and the tendency of these materials to collapse to the minimal spacing, thus excluding large anions such as sulfate and pertechnetate (Figure 4.10).

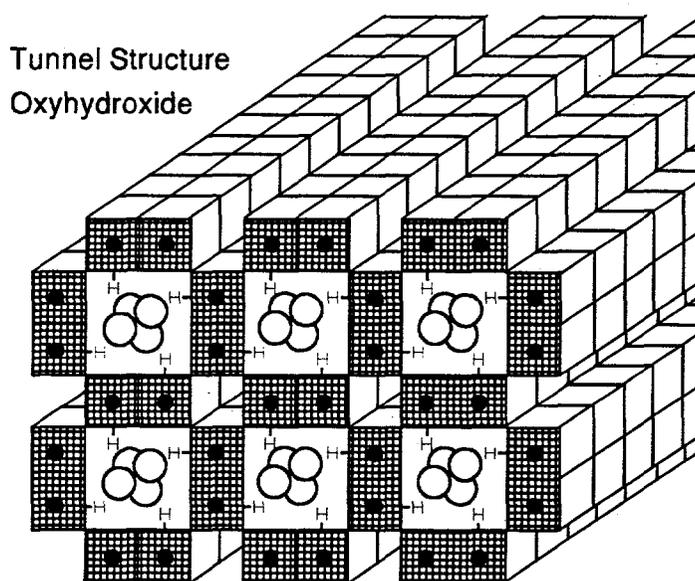


Figure 4.9. Schematic of a Tunnel-Structure Akaganeite-Like Compound Suitable as an Anion-Exchanger for Tetrahedral-Shaped Anions

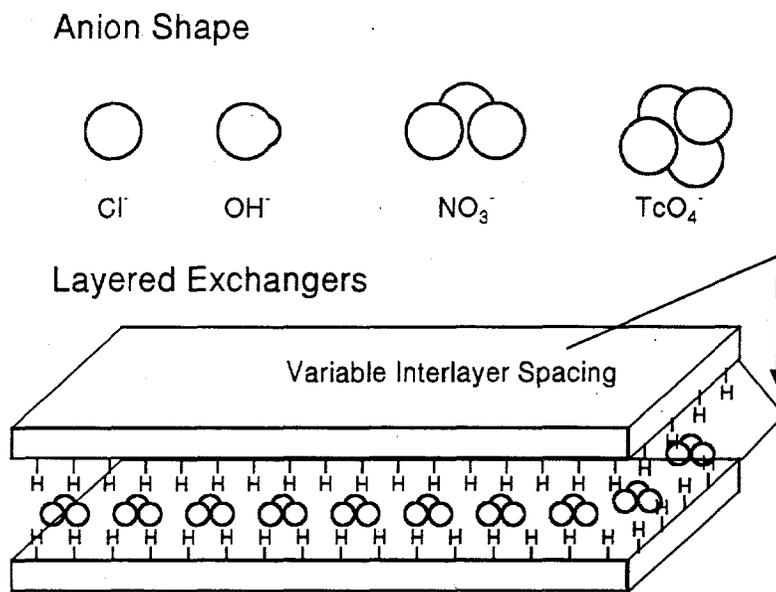


Figure 4.10. Shapes of Anions and the Inherent Selectivity of Layered Exchangers Such as Hydrotalcite for Planar Anions

The known tunnel-structure anion exchangers, however, are not stable for extended periods in low-ionic-strength groundwater solutions and generally transform to other oxyhydroxide phases such as goethite. In contrast, the manganese oxide cation exchangers are quite stable in oxidizing environments. Our approach, therefore, has been to synthesize and test a mixed iron/manganese tunnel-structure oxide in the hope that a compromise between tetrahedral anion selectivity and stability in groundwater can be found. Much of this work is in progress or awaiting analytical results so we will only describe the approach taken.

For cation exchange (largely radium) we synthesized and tested a tunnel-structure manganese oxide to see how the ion exchange selectivities for potassium, rubidium, and barium compared (potassium and rubidium have essentially the same ionic radii as barium and radium, respectively) and are awaiting the analytical results.

For anion exchange (largely technetium), we synthesized a series of tunnel-structure manganese oxides having different amounts of iron substitution. X-ray diffraction results suggest that these syntheses were successful in preserving the tunnel structure. We are further characterizing these materials to identify whether the desired incorporation of structural hydroxyls with increasing iron substitution was also achieved. If the hydroxyls are present, then technetium selectivity tests will be performed.

Lastly, we sent samples of all the manganese and manganese/iron oxides synthesized for analysis by X-ray absorption spectroscopy to determine whether this technique can measure the differences in tunnel diameters that we expect to see.

4.5 Development of a Possible Radium Separation Process

The large quantities of radium ore stored at Fernald are scheduled for vitrification in FY 1998 as a result of a legal record of decision. This ore is a valuable resource, in our opinion, and if a reliable method could be found for separating the radium efficiently, this isotope could find many beneficial uses for the production of short-lived medical isotopes that can be used with monoclonal antibodies to destroy cancer cells.

In its current state, the radium is believed to be in solid solution with BaSO_4 . Any separation process must find a way to dissolve this compound and then separate the radium from the barium. The most difficult step is the separation of barium from radium, due to their similar chemical behavior and ionic radii. We are encouraged, however, by the fact that potassium and rubidium also share similar chemistry and ionic radii, and can be separated by exchange on α -zirconium phosphate. We believe that two other inorganic exchange materials might also have sufficient selectivity to perform the separation of radium from barium (tunnel-structure manganese oxides and high-charge layer silicates).

The proposed process (Figure 4.11) involves: 1) dissolution of the barium-radium sulfate by complexation with DTPA, 2) removal of the sulfate by one of three possible methods (cross-membrane extraction, solvent extraction, or anion exchange), 3) selective removal of barium by ion exchange (most likely an alpha-zirconium phosphate), 4) selective removal of radium by ion exchange (manganese oxide, ZrP, or mica), and 5) recovery of the radium in a suitable form for storage or use to generate medical isotopes. In the laboratory, we have synthesized a batch of BaSO_4 and successfully demonstrated the ability to dissolve it at room temperature and at higher temperatures using DTPA. The results of these tests show that the main factors influencing the rate of dissolution are temperature and pH. At 95°C and a solution pH of 10 or higher, solubilization occurs on the order of minutes. At lower pH or temperature, longer times (as much as 4-5 d at 25°C and pH 10 or higher) are needed. The use of a high-pH solution to dissolve the (barium, radium) SO_4 is not expected to cause difficulties in the sulfate removal step if the liquid membrane or solvent extraction approaches are taken since these are essentially acid-stripping processes anyway. We also have synthesized and begun testing a tunnel-structure manganese oxide for separation of radium from barium.

Contacts were made with WHC, Fernald, and Fluor-Daniel regarding the proposed radium separation process and the use of radium for production of medical isotopes. As a result of these contacts, we gathered further information about the solubility of the DTPA complex for radium (using barium as the analog) as a function of temperature, the kinetics of the dissolution of BaSO_4 using DTPA, and the cost of the DTPA reagent. Vitrification of the Fernald radium ore is scheduled to begin in FY 1998 according to a legal record of decision, and we believe that the method is straightforward enough that with sufficient support we could have a viable full-scale process in place by then.

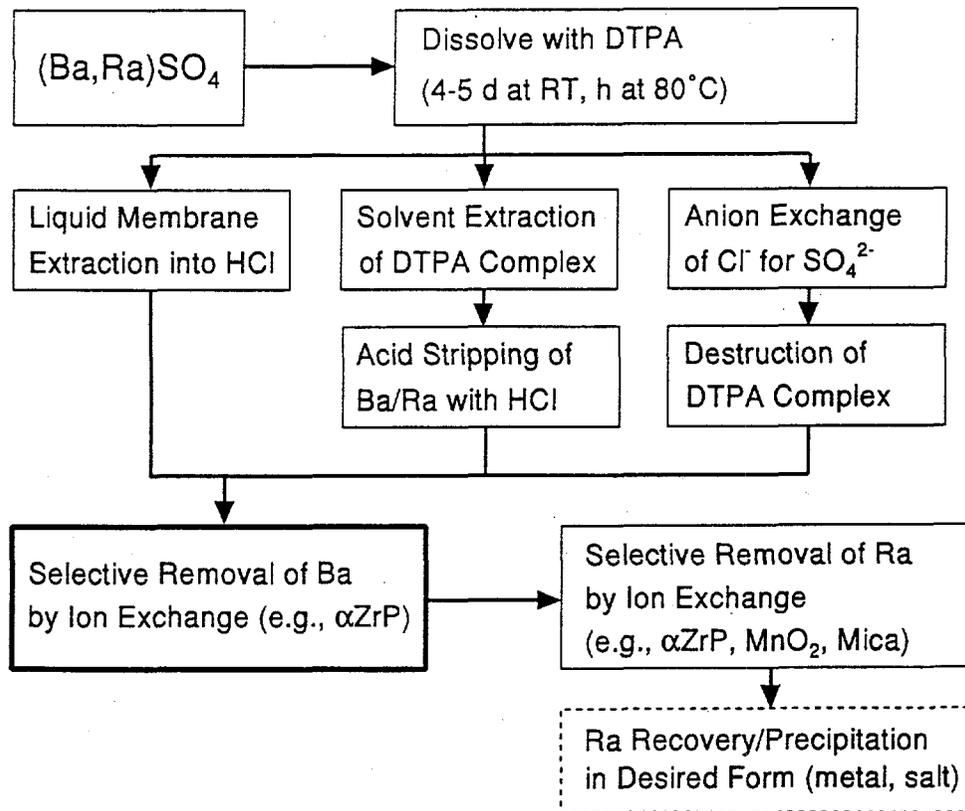


Figure 4.11. Schematic of Proposed Radium Separation Process

4.6 Future Plans

For the remainder of FY 1995 we plan to

- test engineered forms of the CST and Na-TIT samples for strontium selectivity in both groundwater and HLW matrices
- determine binary exchange coefficients for strontium with other cations common in groundwater (i.e., calcium, magnesium, and sodium)
- test several manganese/iron oxyhydroxides and Aliquat-modified zeolites for TcO_4^- selectivity in LLW matrices
- complete our gathering of solubility (DTPA at various pHs and temperatures) and preliminary selectivity ($\alpha\text{-ZrP}$, $\alpha\text{-MnO}_2$, and mica) data to support the proposed radium, separation process.

We note that the results of the FY 1994 testing have already been used to select novel adsorbents for several proposed demonstrations of strontium removal from groundwater at the Hanford Site (e.g., Tegrotenhuis 1994). Our continued testing will strengthen this database.

In FY 1996, we propose to

- continue testing and modeling of engineered forms of strontium ion exchangers in groundwater and HLW matrices
- continue testing of novel anion exchangers for TcO_4^- in groundwater, LLW, and HLW matrices
- refine synthesis and testing of tunnel-structure oxyhydroxide and oxide ion exchange materials optimized for radium and for TcO_4^-
- start development of engineered forms of the radium and TcO_4^- ion exchangers.

5.0 3M/IBC

(T. Kafka, 3M, and R. Bruening, IBC)

Removing the very small quantities of radionuclides present in the waste at Hanford and the other nuclear processing sites will allow the remaining waste to be treated as low-level waste, resulting in major cost savings. This strategy requires separation technologies that are ion specific, operate at high flow rates, operate effectively in the presence of high levels of radiation, concentrate the high-level waste, generate a minimum of secondary waste, and are available in an engineered form. A team of staff from 3M, IBC Advanced Technologies, Inc. (IBC), and PNL was formed by DOE to address the separation of cesium, strontium, and technetium.

5.1 Introduction

3M/IBC initially provided ligands to PNL for testing that were linked to a silica structure for the recovery of cesium or strontium. These powders were then placed in a Teflon web, and fabricated into a filter assembly. Samples of SuperLig[®] web were tested at PNL to determine radiation stability of both the Teflon web and the ligand (see Section 3.5). The Teflon degraded at $< 2E6$ rad; however, both the strontium-specific and the cesium-specific ligands were stable to radiation values of $> 2E7$ rad total dose. Emphasis in FY 1995 has been placed on ligands linked to powders that are more stable in alkaline wastes, TiO_2 or ZrO_2 ; and web materials that are highly resistant to radiation. In addition, SuperLig[®]644 resin has been prepared without linking it to an inorganic powder. Filter assemblies (1 ft²) have been fabricated for testing with simulated and actual waste. Other materials such as pHTiA (cesium) and IONSIV[®] A-51 zeolite (technetium) were placed in webs for testing at PNL, WV, and INEL with excellent results (Kafka 1995).

During FY 1995, a new high-capacity, cesium-specific ligand was developed, major advances were made in the development and processing of a new, radiation and strong alkali resistant membrane, and the efficacy of the technology was demonstrated using acidic, high-level waste in a hot cell at INEL (Bray et al. 1995) and in removing traces of technetium from 360 gallons of low-level waste at the West Valley Demonstration Site. A patent application was filed covering the new membrane.

Plans were made, contingent on funding, to advance the implementation of the technology by conducting a series of increasingly demanding demonstrations during FY 1996.

5.2 Cesium Removal Ligand Synthesis

A new, high-capacity particle, identified as SuperLig®644, was prepared by IBC. IBC produced kilogram quantities of SuperLig®644 polymer, doing the final polymerization in 100-g batches to monitor batch-to-batch variation. The material is being prepared as 20-40 mesh material for column use and ground to a powder for web use.

A major column test was completed in November by a team from PNL, IBC, and 3M (Brown et al. 1995) to compare the performance of SuperLig®644 with other ion exchange resins. These tests used synthetic Hanford NCAW and also tested CS-100 and R-F resins for both loading and elution. The loadings were carried out at 25°C and 9 cv/h. Elution of the cesium was carried out at 0.5 M HNO₃. As shown in Tables 5.1 and 5.2 and Figures 5.1 and 5.2, SuperLig®644 has greater capacity for cesium than either of the other resins. The elution data indicates that it barely absorbs potassium while both of the other resins do and that the volume compression is 30% better than R-F and 100% better than CS-100.

Table 5.1. NCAW Simulant Composition

Species	NCAW, <u>M</u>
Na	5.00
K	0.12
Rb	5.00E-05
Cs	5.00E-04
Al	0.43
SO ₄	0.15
OH (Total)	3.40
OH (Free)	1.68
CO ₃	0.23
NO ₂	0.43
NO ₃	1.67
F	0.089
PO ₄	0.025
Na/Cs Ratio:	1.00E+04
K/Cs Ratio:	240
Na/K Ratio:	42

Table 5.2. Summary of Ion Exchange Material Properties and Results

Material Properties and Results	CS-100	R-F	SuperLig® 644
Resin F-factor (mass dry/mass wet)	0.6353	0.8419	1.000
Resin mass in column "as received" (g)	98.31	91.20	47.12
Resin mass in column "dry basis" (g)	62.46	76.78	47.12
Initial column volume (mL)	220	210	210
Resin particle size (mesh)	20-45	45-70	20-45
Average resin particle size (mesh)	35	60	35
Resin density in NCAW "dry basis" (g/mL)	0.28	0.37	0.22
Cesium loading (mmole Cs/g dry resin)	0.039	0.18	0.20
Cesium loading (mmole Cs/mL resin)	0.011	0.070	0.045
Loading volume (cv) to 0.5 C/C ₀ (λ)	22.5	139	93.6
Elution volume to 0.1 C/C ₀ (cv)	3.2	7.0	3.5
Peak cesium concentration (C/C ₀)	27.8	38.5	185
Volume compression at 0.1 C/C ₀	6.9	20	27
Cesium mass balance	98%	90%	105%
Sodium/cesium in elution composite	78.2	20.6	10.5
Potassium/cesium in elution composite	0.16	0.14	<0.046

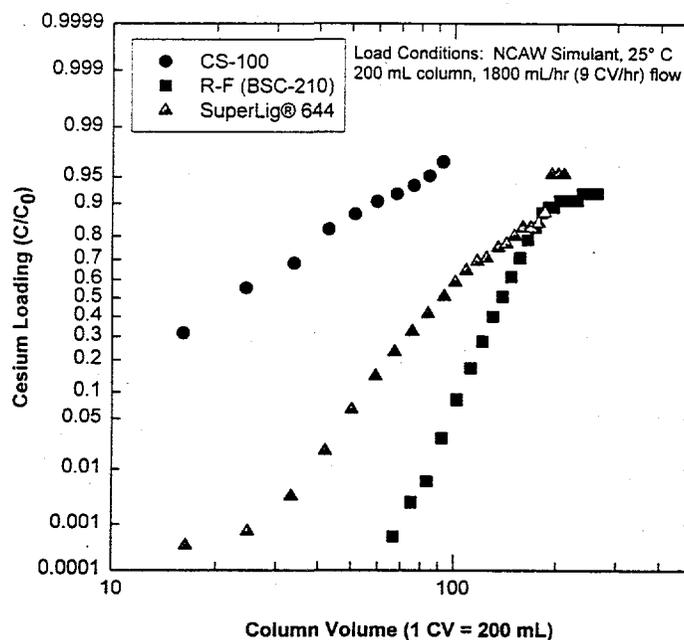


Figure 5.1. Comparison of SuperLig®644, R-F, and CS-100 Resins After Column Loading with NCAW at 9 cv/h (cv = 200 mL) at 25°C

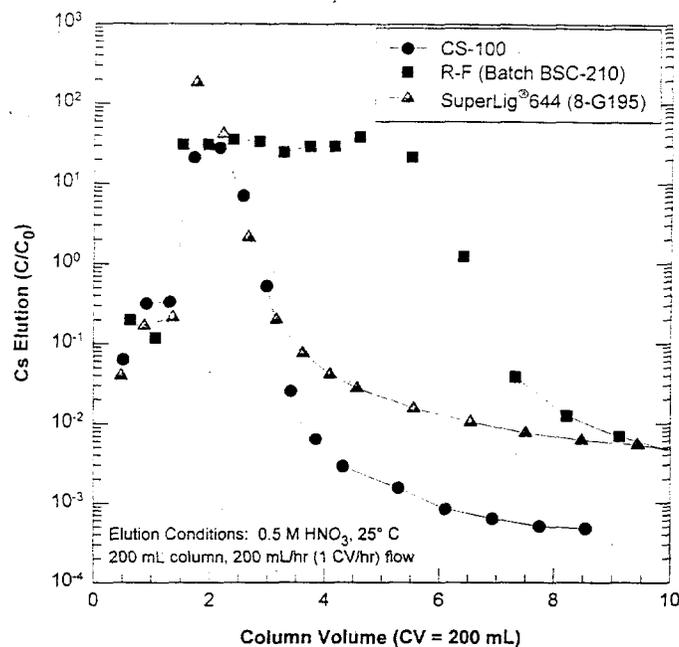


Figure 5.2. Comparison of SuperLig®644, R-F, and CS-100 Resins After Column Elution with 0.5 M HNO₃ at 1 cv/h (cv = 200 mL) at 25°C

Work is continuing on the development of an equivalent to uncured SuperLig®644 (which showed excessive resin expansion when converted to the Na⁺ form) which can be used continuously without the generation of excessive pressure. Cured SuperLig®644 (heat-treated) resin was delivered to PNL and 3M for testing. A batch of the resin (20-50 mesh) was also produced for testing at ORNL for the removal of cesium from Melton Valley waste. Work also continued to produce a cartridge using WWL membrane and SuperLig®644. Additional work is required before initiating repeated cycle tests on cartridges to determine the chemical stability of the new cesium exchanger.

5.3 Membrane Development

A membrane, WWL, has been developed based on Kevlar™, which provides the same separation characteristics as Empore™ membranes while providing durability at high levels of radiation and exposure to strongly alkaline, pH 14 conditions. A patent application covering this material has been filed.

The first samples of WWL/Kevlar™ membrane containing SuperLig®644 were produced and tested for separation of cesium from NCAW waste (see Figure 5.3). PNL determined that the membrane was stable during irradiation up to 2.0E+09 rad. A patent application was filed on the radiation-stable WWL membrane. Testing has shown that a WWL membrane is a more "open" structure than a

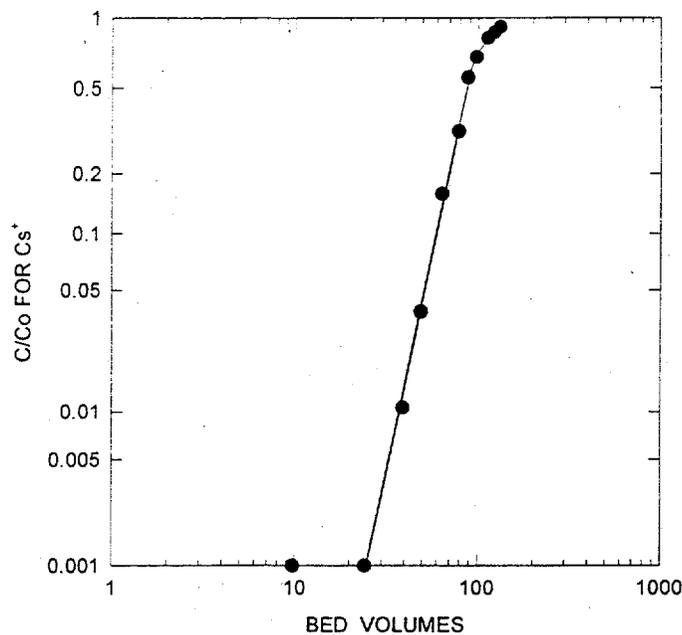


Figure 5.3. Removal of Cesium from a 66-ppm Level NCAW Solution Using a SuperLig®644 3M Membrane

comparable Empore™ membrane. This enables it to be used to process "solutions" containing fine particulates which result in the plugging of an Empore cartridge.

Pilot line and process modifications were developed so that membrane can be produced continuously, providing the basis of a manufacturing process.

5.4 Hot Cell Testing

PNL, 3M, and IBC, working with INEL staff, demonstrated the removal of strontium and cesium from radioactive acidic tank waste using 3M membrane technology (Bray et al. 1995). The acidic waste experiments duplicated initial mimic "cold" waste results and show that both nuclides can be removed to very low concentrations. Figure 5.4 shows removal of ¹³⁷Cs using a titanium phosphate adsorbent (PhTiA). The adsorbent had high capacity despite the presence of sodium and potassium at high concentrations relative to cesium. Similar results were obtained for the removal of ⁹⁰Sr and lead using IBC SuperLig™ technology (Figure 5.5) The tests also confirmed the efficiency of fine particle-web technology. This same technology can be applied to numerous other adsorbents that have been prepared as fine particles, too fine for use in standard ion exchange columns because they would create too much back pressure. Other adsorbents, which are large enough for column use, can be ground to a finer size and incorporated into membranes. They can then be used at much higher flow rates to achieve more rapid separations.

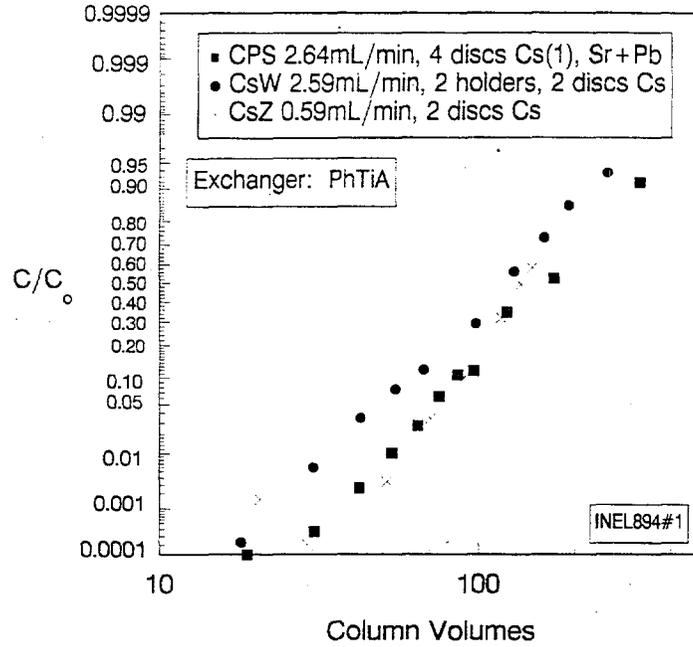


Figure 5.4. Removal of ¹³⁷Cs from ICPP Tank WM-185 Acid Waste with the Use of PhTiA Ion Exchange-Web Technology

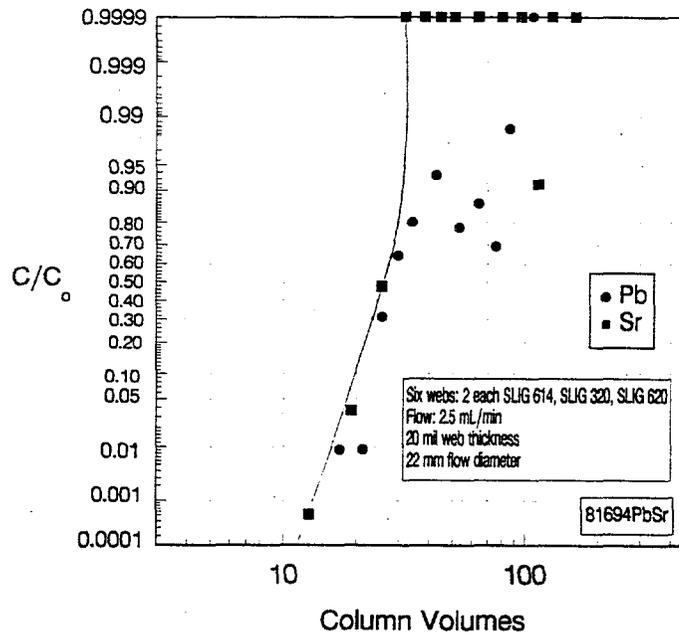


Figure 5.5. Removal of ⁹⁰Sr from ICPP Tank WM-185 Acid Waste with the Use of SuperLig[®] Ligand-Web Technology

5.5 West Valley Demonstration

In FY 1994, PNL became aware of a need at the West Valley Demonstration Project (WVDP), in West Valley, New York, for removing ^{99}Tc from the plant liquid effluent. Following a 3M/PNL staff visit to WV for discussions with plant personnel, 3M loaded a PNL-recommended exchanger into a silica web for testing. The O2 Facility wastewater contains $4.4\text{E-}7\text{g Tc/L}$ or approximately $7.5\text{E-}6\ \mu\text{Ci/mL}$ of ^{99}Tc . Initial batch distribution tests at WVNS with samples of PNL-prepared ion exchanger based on AliquatTM336 and plant water showed that this was an effective method of removing technetium.

Additional tests have now demonstrated the superiority of activated carbon over silica as the carrier for the extractant. In fact, carbon by itself was shown to retain the ReO_4^- anion (cold stand-in for Tc), Figure 5.6. Additional studies were also conducted at Pace Laboratories using TcO_4^- . Hardware components were purchased (including pumps) and two systems were assembled. One system was sent to WV for installation during the first week in January. During the proposed WV test, a side stream of plant effluent was to be passed through the 3M/PNL-designed system (0.1 gpm or 1/40th of the plant stream). On the successful completion of the initial phase, WVDP would then evaluate the purchase of a larger 3M cartridge system for treatment of the full effluent stream.

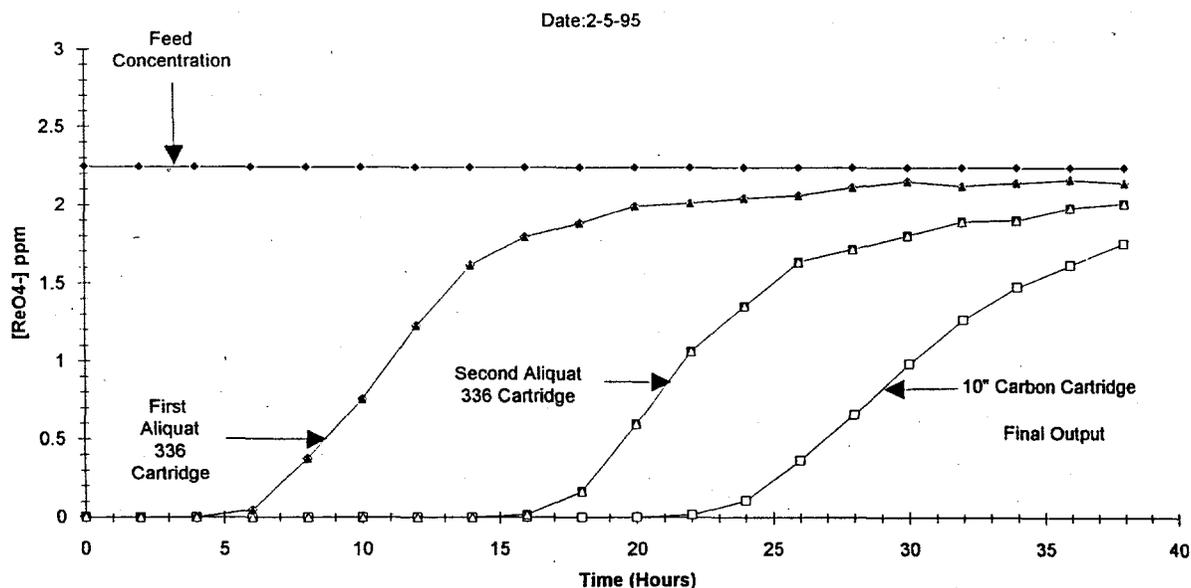


Figure 5.6. Loading of ReO_4^- in a Three-Cartridge Web System to Simulate West Valley O2 Facility Water

A test stand (Figure 5.7) was delivered to WVNS and operated for a cumulative 60 h, processing 360 gallons of water and achieving a technetium decontamination factor of >10 as required. The original equipment included a pump, a prefilter, two separation cartridges each containing 1 ft² of an Empore™ membrane loaded with carbon coated with Aliquat™ 336 as the adsorber, and a post filter. Initial experiments were prematurely terminated due to plugging of the prefilters.

It was found that the various prefilters that had worked in extensive pretrials at 3M were insufficient to handle the fines in the waste stream at WV for an extended period without high-pressure buildup. Testing showed that calcium and magnesium were present (hard water), and aluminum, consistent with zeolite fines and a carbon fluorine ratio (probably caused by the algae in the water), was also measured.

A series of long-term filter experiments were set up at 3M with prefilters in series with a WWL cartridge loaded with carbon-treated Aliquat™ 336. In each case, the WWL cartridge was used to remove perrhenate from a standard solution and tap water at 18 gallons per minute (1 ft² of surface). The first experiment was run for 32 days using a Pall 0.1- μ m prefilter that was replaced 8 times, treating 13,824 gallons of water. The second experiment involves inserting a 3M 2- μ m filter in front of the Pall filter. In 23 days the Pall filter only had to be changed twice, showing a significant improvement. However, this is only a indication of how the WV water may perform during the actual test.

Two experiments were also run using cartridges loaded with WVN resin (a possible replacement for carbon/Aliquat™ 336) in WWL membrane that had previously given outstanding separation performance. In each case, premature perrhenate breakthrough occurred. This membrane is weaker than membrane loaded with carbon or SuperLig®644 and it is believed that it was damaged during the cartridge manufacturing step. A more resilient membrane was developed.

The 02 Facility zeolite columns in the WV system are currently being reloaded and so the 3M/PNL experiment planned for May was postponed until July.

5.6 Cross-Program Interactions

The versatility of 3M's membrane technology enables it to be used to enhance the practical performance of particles developed or used in other parts of the ESP. Numerous interactions between sites continued during the year. Examples follow.

- SuperLig processing was reviewed in Provo, Utah, with 3M manufacturing staff, and arrangements were made for IBC to use larger-scale processing equipment at 3M (the first experiment was initiated on April 5).

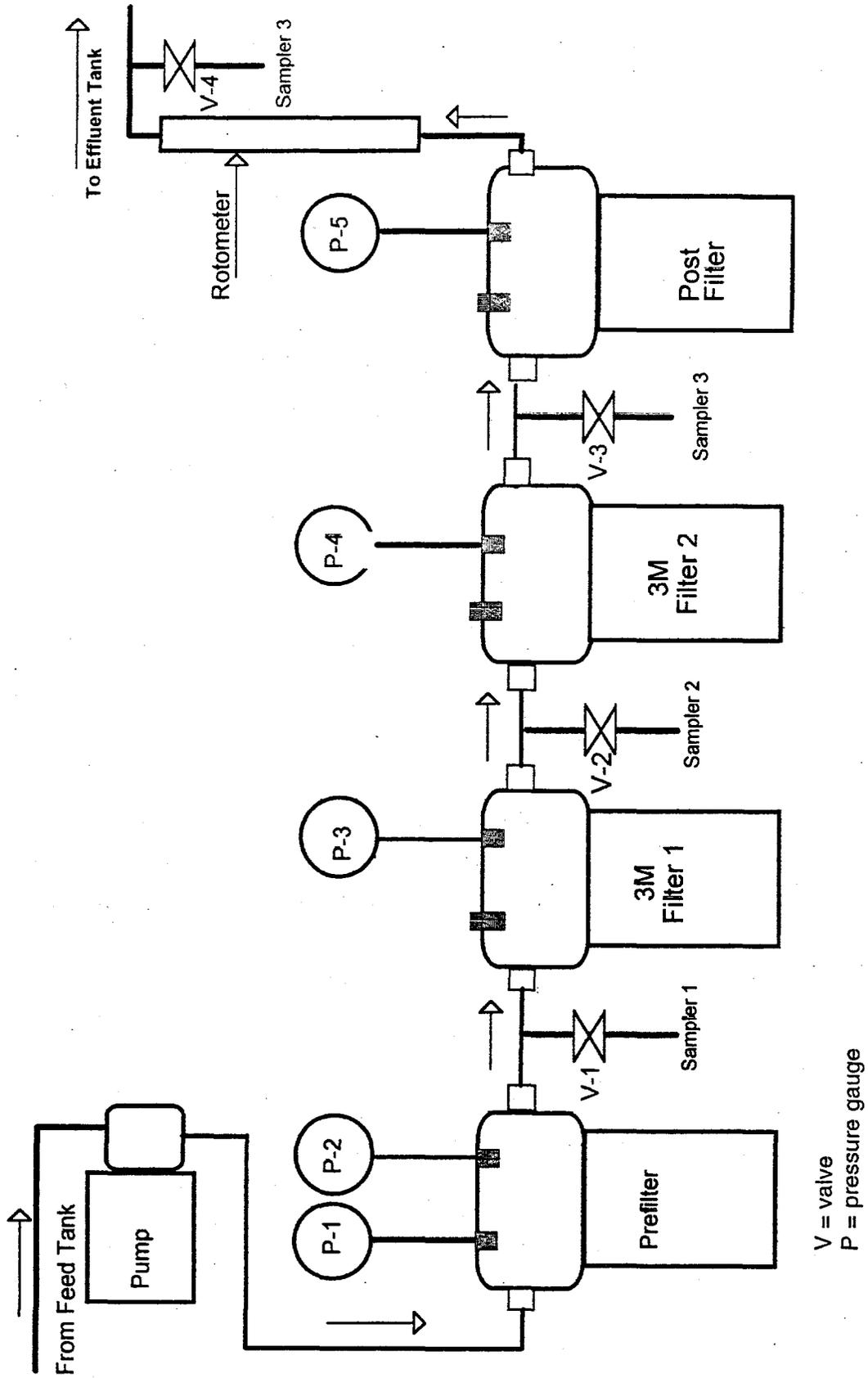


Figure 5.7. Equipment Design for ⁹⁹Tc Removal at the West Valley 02 Facility Water

- 3M staff visited INEL to initiate experimental work similar to that at WV, cesium removal from the TSF-05 injection well. A 1-in. sample of web containing potassium cobaltihexacyanoferrate (PCHF) was tested using 1 L of INEL TSF-05 well water with complete removal of the cesium. Sodium titanate developed by AS/Texas A&M was incorporated in Empore™ membrane and had excellent performance for adsorbing strontium. Plans were made for accelerating the cesium and strontium separation demonstration. Supplies and a materials list were sent to INEL in preparation for a prefiltration demonstration experiment planned for late July. Initial experiments were run in preparation for the scale-up of the manufacture of PCHF for use at Well TSF-05.
- The 3M/PNL/ESP work was reviewed in Washington, D.C., on March 22 for the National Research Council Board on Radioactive Waste Management, Committee on Environmental Management Technologies.
- Potassium cobaltihexacyanoferrate, used by ORNL to remove cesium from solutions up to a pH of 12, was similarly found to give outstanding results when placed in 3M webs. Additional batches of PCHF were produced. A sample was incorporated as an Empore membrane and provided to ORNL for their groundwater/cesium removal study.
- Empore™ membranes containing R-F resin, TevaSpec, and sodium titanate were supplied to Savannah River to develop a method of sample preparation in which radioactive materials are adsorbed on an Empore membrane at an experimental site and then only the membrane is forwarded to a central laboratory for analysis. In this particular application ocean water is being tested and the intention is to eliminate the very costly shipment of large volumes of water containing trace amounts of cesium, technetium, and plutonium.

5.7 Meetings and Site Visits

Papers were given at the American Nuclear Society's 1995 International High Level Radioactive Waste Management Conference at Las Vegas and at the Air and Waste Management Conference of Challenges and Innovations in the Management of Hazardous Waste in Washington, D.C.

3M and IBC staff participated in the ESP program review in Washington, D.C., and reviewed the 3M program in St. Paul for a representative of Dames and Moore, DOE Hanford field office.

A visit was made to Hanford to discuss a demonstration of the use of active cartridges to remove cesium from alkaline waste in the 242-A Evaporator; to discuss a demonstration for the removal of cesium, strontium, and technetium from groundwater in the N-Springs area; and to hold the quarterly meeting with EM-30 personnel. Two videoconferences were also held to discuss the 242-A Evaporator demonstration.

The next steps in the Environmental Sampling Demonstration and a multicontaminant separation in the "R" Reactor Basin were discussed during a visit to Savannah River.

A visit was made to Hanford May 31 - June 1 to attend the DOE Tank Waste Remediation System (TWRS) Privatization meeting, to review current 3M program plans and future plans with PNL staff and personnel at the DOE field office, and to continue discussions concerning the two demonstrations being planned at Hanford.

6.0 AlliedSignal/Texas A&M

(S. Yates, AS, and A. Clearfield, Texas A&M)

AlliedSignal (AS) has a subcontract with Texas A&M, specifically Professor A. Clearfield and his team. As materials are developed, they are transferred to AS for further testing, commercialization, and characterization. As samples are prepared by either AS or Texas A&M, they are sent to PNL for evaluation. This includes chemical and radiation stability, tracer studies with synthetic wastes, and selected tests with actual wastes.

AS/Texas A&M have prepared samples of sodium titanate in the powder form and have discovered a binder that is radiation and caustic stable. Engineered form sodium titanates show strontium values equal to that of the powders. In addition, a series of cesium-specific compounds, such as synthetic micas, are being investigated, which should provide enhanced separation of cesium over potassium.

A milestone report was completed during the year entitled *Cesium and Strontium Ion Specific Exchangers for Nuclear Waste Effluent Remediation* (Yates et al. 1994). This report summarizes work on the development of novel ion exchangers for cesium and strontium over the FY 1994 time period. The program has three tasks: 1) exchanger screening, 2) exchanger preparation, and 3) exchanger testing.

6.1 Exchanger Screening

Screening activity is focused on development of better sodium titanates for strontium ion exchange, and on development of new materials for cesium ion exchange (Clearfield et al. 1995; Clearfield 1995). In the latter activity, several promising leads were established, including the preparation of phlogopite micas under hydrothermal conditions from simple monomeric starting materials, and a new procedure for removing potassium from natural or synthetic micas that avoids the use of expensive sodium tetraphenylborate. Nonmica exchangers were also identified that promise even higher selectivity for cesium over potassium and sodium.

Screening activities for cesium exchangers have focused on the modification of micas for increased potassium resistance. The new result is that some of the micas can selectively complex the tetraphenylborate ion, which increases dramatically the affinity of these materials for cesium. Micas with increased layer charge have also been prepared.

AS/Texas A&M succeeded in preparing sodium phlogopite from natural mica phlogopite by successive hydrothermal treatments with strong (1-2 M) sodium chloride solutions. The ion exchange behavior of this product at several levels of sodium replacement were examined as to Cs⁺ uptake from

high sodium-containing solutions. Although the mica showed a high affinity for Cs^+ , the K_d values were lower than those obtained with the amine exchanged biotite. Further work to boost the K_d values is in progress.

A new microporous sodium zirconium silicate was prepared hydrothermally. Previously we had prepared a layered sodium zirconate in a similar fashion but without sodium silicate. The K_d values of both exchangers in 0.001 M alkali and alkaline earth cation solutions were determined. The uptake of alkali metal cations was in the order $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Li}^+$ (but the K_d values were low (1220 mL/g for Cs^+). Values for Sr^{2+} and Ba^{2+} were reasonably high.

Titration data as well as K_d values determined in 5 M sodium nitrate/1 M sodium hydroxide solutions show that the capacity of CST type compounds for Cs^+ is less than 0.1 meq/g. High K_d values are obtained only if this low capacity is not exceeded. Thus, an inordinate amount of exchanger would be required to remediate Hanford waste solutions. Use of this exchanger would then increase the number of glass logs to encapsulate the Cs^+ severalfold, as the Cs^+ cannot be completely removed from the CST.

Texas A&M developed a tetraphenylborate (TPB)-mica complex that completely precipitates Cs^+ from high Na^+ solutions. By simply washing the mica- Cs^+ TPB complex, the Cs^+ diffuses into the mica, reforming the sodium TPB which can be recovered and reused. The Cs^+ mica traps the Cs^+ permanently and it may be possible to eliminate the log making step. Potassium ion behaves the same way, but Cs^+ is preferred. Efforts to increase the selectivity for Cs^+ over K^+ by alteration of the structure of the boron ligand are in progress. New vanadyl-pillared micas have been prepared for cesium ion exchange. These materials have properties similar to, but somewhat better than the zirconia-pillared micas reported earlier. XRD and surface area analyses are reported.

In the area of cesium removal for acid wastes, a new phosphate-type ion exchanger was developed based on modification of alkaline titanium phosphates. This ion exchanger can be prepared as a granular material, and shows a K_d for Cs of 25,000 mL/g from 0.1 M nitric acid. Capacities are expected to be high. Optimization of this material is in progress, along with testing at various acid concentrations, etc., to understand the scope of utility of the material. We plan to scale up this process as soon as this optimization is complete. The preparation of this material was requested by PNL in the revised statement of work, and was based on the success of PhTiA used at INEL for cesium recovery from acid wastes.

6.2 Exchanger Preparation

The preparation of sodium titanate was successfully scaled up to the 10-kg scale, and produced an ion exchanger with a K_d of 20,000 mL/g in 5 M sodium nitrate/ 0.1 M hydroxide. Studies were completed on the fluid dynamics of the preparation mixture which should allow further scaleup without difficulty. New pillared micas were developed that are more resistant to potassium poisoning than the amine biotites developed in previous work, but the capacity and selectivity of these materials are lower

than these prior materials. A new pelletization method was developed that can be used for both cesium and strontium exchangers. For both cesium and strontium, the new method enhances the selectivity of the parent powder and preserves its capacity.

Sodium titanate powder and bound sodium titanate have been evaluated as a function of solution hydroxide concentration and sodium concentration. The results show that the pattern of responses to these variables is similar to that of the earlier generation sodium titanate tested by PNL, and that binding does not change this pattern. The sole exception is that bound sodium titanate is less effective than unbound sodium titanate at low hydroxide concentrations.

In other work, substantial progress was made in learning to bind sodium titanate using a second-generation binder that is much more mechanically strong than previous materials. The new process delivers extrudates that survive for extended periods under agitation in caustic without attrition or loss of weight. AS has developed an improved procedure for making pellets with improved mechanical strength. Since then we have worked to adapt this procedure to the use of a motorized pellet former that will allow us to make reasonable quantities of pellets rapidly. The pellets have so far been tested only for mechanical strength. Using an Instron-based crush strength, they are 30-50% stronger than our control, UOP's AW-300 1/16-in. extrudates. Earlier hand-made pellets were shown to retain their high Kd values through the pelletization process, and this will be verified for the machine-prepared product.

6.3 Exchanger Testing

Distribution constant and capacity measurements were made with both cesium and strontium exchangers, and column studies were completed with both materials. Among the highlights of this work were the demonstration that AS strontium exchanger maintains its high selectivity in the presence of complexants such as oxalic or citric acids and EDTA, and that the capacity of this pelletized exchanger for strontium under dynamic column conditions is 2.0 meq/g (from 47.2 ppm Sr, 5 M sodium nitrate, 0.1 M sodium hydroxide feed). Our amine biotite has a static capacity of only 0.08 meq/g (from 60 ppm Cs, 5 M Na⁺, 1 M OH⁻ feed). Column studies (DeFilippi and Yates 1994) with the latter material after pelletization under column conditions showed that it has good mass transfer kinetics.

Column trials were completed using TiP-bound zirconium biotite and TiP bound sodium titanate. The unit was constructed using 1-in. ID columns and appropriate pumping and monitoring systems for these larger scale experiments. The zirconium biotite series was completed using NCAW simulant as the feed. At 1.2 cv/h feed flowrate, breakthrough occurred after 4 cv. The fast breakthrough is not caused by the presence of binder but by the low capacity of the zirconium biotite (ca. 0.06 meq/g).

A milestone letter report was completed that summarized the characterization of cesium and strontium exchangers via column experiments (DeFilippi and Yates 1994). AS has determined how the bound cesium and strontium exchangers perform in larger-scale column operation (1-in. diameter). As

expected, the cesium capacities for AS non-optimized TiP-bound Zr-biotite were low (0.026 meq/g). However, the binder held up in the caustic environment of the Hanford NCAW feed. The bound exchange particles also withstood very high flow rates (135 cv/h, or 25 cm/min). Efforts are under way to increase the capacity of zirconium-biotite, while maintaining its high selectivity for cesium over potassium.

The TiP-bound sodium-titanate performed very well for strontium uptake under column conditions. With the high capacity of the bound sodium-titanate (2 meq/g), we were able to treat 600 cv of strontium feed (5.1 M Na, 0.1 M OH⁻, and 47.2 ppm strontium) at a feed rate of 7.2 cv/h. As in the case above, the TiP-bound sodium-titanate exchange particles remained intact throughout the column tests.

Under the column conditions tested, a theoretical plate analysis shows that both the cesium and strontium exchangers are limited by particle diffusion. We can increase the rate of particle diffusion by operating the columns at slower feed rates. By enhancing the capacity of zirconium-biotite, the driving force for cesium to enter the exchanger would increase, thereby also increasing the rate of particle diffusion.

6.4 Cross-Program Interactions

AlliedSignal is currently at various stages of seven outside evaluations of bound or unbound sodium titanate materials. Preparation of samples for demonstrations has become a significant activity. Samples were sent to PNL, LANL, and 3M, and test results were reported at the recent program review meeting. Currently, AS is preparing a 1-kg sample of bound sodium titanate for PNL, and has continuing activities with LANL, 3M, and Savannah River. These are summarized briefly below

- **Strontium in Groundwater (PNL):** This study, completed by J. E. Amonette in 1994, showed that sodium titanate is an effective adsorbent for strontium in groundwater. Exchangers in this study included the CST, various zeolites and our sodium titanate, and K_d appeared to be strongly influenced by particle size.
- **Strontium in the Presence of Complexants (LANL):** F. Marsh reports that AS sodium titanate was the second best exchanger he tested for sorption of strontium from untreated organic containing simulant. He measured a K_d of 248 mL/g for strontium and of 38 mL/g for americium. When measures were taken to treat the simulant hydrothermally, or with irradiation, K_d s for strontium increased to near normal values (16,000 and > 18,000 mL/g). The K_d for americium increased also. At his request, AS also sent F. Marsh an additional small sample for testing with plutonium.
- **Sodium Titanate as a Substrate for Empore Membranes (3M):** T. Kafka's team has prepared Empore membranes containing our sodium titanate powder. Using a simulant containing 60 ppm strontium in 6 M sodium nitrate/0.1 M sodium hydroxide, they obtained breakthrough

curves showing rapid uptake and high capacities. A total of 800 cv of feed were passed through their membrane before the strontium concentration became detectable.

- Sodium Titanate K_d Study (PNL): PNL is currently measuring K_d s for a number of elements on sodium titanate powder prepared for them last year. This study will include some measurements with actual Hanford waste (DSSF).
- Strontium in the Presence of Complexants (PNL): We are currently preparing a large sample of bound sodium titanate for PNL, which will be used to complete column studies of strontium adsorption in the presence of organic complexants. This may also include tests with actual waste.
- NaTi for Savannah River and 3M: AS completed a confidentiality agreement with Savannah River to allow D. McCabe to complete a series of studies of sodium titanate with strontium alkaline waste for the removal of strontium and plutonium. Samples were prepared and shipped for evaluation to Savannah River, who requested only 5 g of material, which was generated by a relatively tedious process of hand-grinding and sieving. Because it is essentially impossible by this method to remove $< 1 \mu\text{m}$ fines by sieving or filtration, and developed a procedure based on settling time which works well. The sample has been successfully prepared and shipped. 3M requested much larger quantities (500-1000 g) of the same fine powder. Because the procedure used before would have been extremely tedious to run for so much sample, we obtained on loan a sophisticated grinding mill that can produce fine powders readily. Preliminary particle size analysis results show that this mill can prepare samples that should be acceptable to 3M, and this material has been shipped to 3M.
- Strontium at ORNL: A confidentiality agreement has been completed with ORNL to cover one or possibly two evaluations there. AS anticipates beginning work with ORNL soon.

7.0 Conclusions

A collaborative effort between PNL and industry/university participants has been under way since FY 1992. In conjunction with the two contracts (AS and 3M), PNL continues to be involved in other areas of research directed toward the same goals. These include, for examples, interaction with industry, academia, and the national laboratories in the study and understanding of binders and alternative web systems; the testing and interaction with 3M and AS as they prepare new materials for testing; the evaluation of other ion exchange materials being tested with simulated and actual Hanford wastes; and the initial evaluation for testing engineered systems with actual wastes from INEL, West Valley, ORNL, and Hanford. Two onsite demonstrations were initiated or completed during the year; the 3M/IBC web system has been tested at INEL using acid radioactive waste (Bray and Brown 1995); and testing has been initiated at the West Valley Demonstration Facility to remove technetium from waste water using a 3M filter cartridge system.

8.0 References and Presentations

8.1 References

- Bigham, J. M., L. Carlson, and E. Murad. 1994. "Schwertmannite, a New Iron Oxyhydroxy-Sulphate from Pyhäsalmi, Finland, and Other Localities." *Mineral. Mag.* 58:641-648.
- Bray, L. A., G. N. Brown, D. Anderson, L. R. White, T. M. Kafka, R. L. Bruening, R. M. Decker, L. C. Lewis, and C. Lundholm. 1995. *Web Technology in the Separation of Strontium and Cesium from INEL-ICPP Radioactive Acid Waste (WM-185)*. PNL-10283, Pacific Northwest Laboratory, Richland, Washington.
- Bray, L. A., and L. L. Burger. March 1994. "Method for Aqueous Radioactive Waste Treatment." U.S. Patent 5,298,166. Pacific Northwest Laboratory, Richland, Washington.
- Brown, G. N., L. A. Bray, R. J. Elovich, L. White, T. Kafka, R. Bruening, and R. Decker. 1995. *Evaluation and Comparison of SuperLig[®]644, Resorcinol Formaldehyde and CS-100 Ion Exchange Materials for the Removal of Cesium from Simulated Alkaline Supernate*. PNL-10486, Pacific Northwest Laboratory, Richland, Washington.
- Bryan, S. A., S. R. Adami, L. A. Bray, C. D. Carlson, J. R. DesChane, R. J. Elovich, and M. R. Telander. 1993. *Radiation Testing of Organic Ion Exchange Resin, CS-100*. TWRSP-93-073, Pacific Northwest Laboratory, Richland, Washington.
- Bryan, S. A., L. R. Pederson, R. D. Scheele, J. L. Ryan, and J. M. Tingey. 1992. *Slurry Growth, Gas Retention and Flammable Gas Generation by Hanford Radioactive Waste Tanks: Synthetic Waste Studies, FY-1991*. PNL-8169, Pacific Northwest Laboratory, Richland, Washington.
- Byström, A. and A. M. Byström. 1950. "The Crystal Structure of Hollandite, the Related Manganese Oxide Minerals, and α -MnO₂." *Acta Crystallogr.* 3:146-154.
- Carlson, C. D., S. R. Adami, L. A. Bray, G. N. Brown, S. A. Bryan, K. J. Carson, J. R. DesChane, R. J. Elovich, and M. R. Telander. 1994. *Supernatant Treatment Technology Development: Report for the Second Quarter FY 1994*. TWRSP-94-031, Pacific Northwest Laboratory, Richland, Washington.
- Clearfield, A. 1995. "Inorganic Ion Exchangers: A Technology Ripe for Development." *Ind. Eng. Chem.*, in press.
- Clearfield, A., L. Bortun, A. I. Bortun, and R. A. Cahill. 1995. "The Use of Inorganic Ion Exchangers for Nuclear and Industrial Waste Remediation." Presented at the Waste Policy Institute Air and Waste Management Assoc. Conference, Washington, D.C., May 10-12, 1995.

DeFilippi, I.C.G. and S. F. Yates. 1994. *Characterization of Cesium and Strontium Exchangers Via Column Experiments*. AlliedSignal Corporation, Des Plaines, Illinois.

Havlin, J. L., D. G. Westfall, and S. R. Olsen. 1985. "Mathematical Models for Potassium Release Kinetics in Calcareous Soils." *Soil Sci. Soc. Amer. J.* 49:371-376.

Kafka, T. M. 1995. *Separation Technologies for Cesium and Strontium*, Phase III Second Period Technical Report (July 1 - December 31, 1994). 3M New Products Department, St. Paul, Minnesota.

Kurath, D. E., L. A. Bray, K. P. Brooks, G. N. Brown, S. A. Bryan, C. D. Carlson, K. J. Carson, J. R. DesChane, R. J. Elovich, and A. Y. Kim. 1994. *Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids*. PNL-10187, Pacific Northwest Laboratory, Richland, Washington.

MacKay, A. L. 1962. " β -Ferric Oxyhydroxide-Akaganeite." *Mineral. Mag.* 33:270-280.

Marsh, S. F., Z. V. Svitra, and S. M. Bowen. 1995. *Effects of Soluble Organic Contaminants and Their Degradation Products on the Removal of Selected Radionuclides from High-Level Waste*. LA-1243, Los Alamos National Laboratory, Los Alamos, New Mexico.

Miyai, Y., K. Ooi, and S. Katoh. 1988. "Recovery of Lithium from Seawater Using a New Type of Ion-Sieve Adsorbent Based on $MgMn_2O_4$." *Sep. Sci. Technol.* 23(1-3):179-191.

Miyata, S. 1983. "Anion-Exchange Properties of Hydrotalcite-Like Compounds." *Clay Miner.* 31:305-311.

Ooi, K., Y. Miyai, and S. Katoh. 1987. "Lithium-Ion Sieve Property of λ -Type Manganese Oxide." *Solvent Extract. Exch.* 5(3):561-572.

Pourbaix, M. 1974. "Atlas of Electrochemical Equilibria in Aqueous Solutions." National Association of Corrosion Engineers, Houston, Texas, pp. 493-503.

Sagara, F., B.-N. Wang, and I. Yoshida. 1989. "Preparation and Adsorption Properties of λ - MnO_2 -Cellulose Hybrid-Type Ion-Exchanger for Lithium Ion." Application to the Enrichment of Lithium Ion from Seawater." *Sep. Sci. Technol.* 24(14):1227-1243.

Tegrotenhuis, W. E. 1994. "Investigating Super-Adsorbents as Part of the 200-BP-5 OU Groundwater Treatability Testing." Presentation to Westinghouse-Hanford Corporation and Bechtol-Hanford Corporation personnel, September 2, 1994.

Tsuji, M. and M. Abe. 1984. "Synthetic Inorganic Ion-Exchange Materials XXXVI. Synthesis of Cryptomelane-Type Hydrous Dioxide as an Ion-Exchange Material and Their Ion-Exchange Selectivities towards Alkali and Alkaline Earth Metal Ions." *Solvent Extract, Exch.* 2(2):253-274.

Tsuji, M., S. Komarneni, Y. Tamaura, and M. Abe. 1992. "Cation Exchange Properties of a Layered Manganic Acid." *Mater. Res. Bull.* 27:741-751.

Turner, S., and P. R. Buseck. 1981. "Todorokites: A New Family of Naturally Occurring Manganese Oxides." *Science* 212:1024-1027.

Yates, S. F., A. Clearfield, I.C.G. DeFilippi, and R. H. Sedeth. 1994. *Cesium and Strontium Ion Specific Exchangers for Nuclear Waste Effluent Remediation*, Final Report - Phase III (through 1994), AlliedSignal Corporation, Des Plaines, Illinois.

8.2 Presentations

The following papers were presented at the 1995 Annual Technical Exchange Meeting in Gaithersburg, Maryland, January 24-26, 1995

- "A Historical Overview of Ion Exchange Materials and Delivery Systems for the Recovery of ^{90}Sr and ^{137}Cs ", L. A. Bray, PNL.
- "Evaluation and Comparison of SuperLig[®] 644, Resorcinol-Formaldehyde and CS-100 Ion Exchange Materials for the Removal of Cesium from Simulated Alkaline Supernate." G. N. Brown, L. A. Bray and R. J. Elovich (PNL); R. L. Bruening and R. M. Decker (IBC); and T. M. Kafka and L. R. White (3M).
- "Inorganic Ion Exchange for Cesium and Strontium," S. Yates (AS), A. Clearfield (Texas A&M).
- "Novel Cesium, Strontium, and Technetium Ion Exchange Membrane," T. M. Kafka (3M), R. L. Bruening (IBC).
- "Design Basis for Metal-Selective Ligands: Molecular Modeling Approach," B. P. Hay (PNL).

Kafka, T. M. (3M), L. A. Bray (PNL), R. L. Bruening (IBC), L. C. Lewis (INEL), and G. Smith (WVNS). 1995. "Use of Novel Solid-Phase Extraction Membranes for Removal of Specific Radionuclides from Nuclear Wastes," Air and Waste Management Association, Waste Policy Institute, Washington, D.C., May 10-12, 1995.

White, L. R. (3M), T. M. Kafka (3M), L. A. Bray (PNL), R. L. Bruening (IBC), L. C. Lewis (INEL), and G. Smith (WVNS). 1995. "Use of Novel Solid-Phase Extraction Membranes for Removal of Specific Radionuclides from Nuclear Wastes," 1995 International High-Level Radioactive Waste Management Conference, May 15, 1995, Las Vegas, Nevada.

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