SPECIALIZED SEPARATIONS UTILIZING 3M MEMBRANE TECHNOLOGY

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ABSTRACT

In response to the need for detection and removal of dissolved contaminants in aqueous sources and wastes, particle-loaded membrane technology has been developed to produce sampling/analytical and large-scale decontamination systems. Benefits of this technology include:

- The use of smaller particles which allows for more efficient removal at higher flow rates
- The membrane/resin matrix prevents channeling of liquids and loss of efficiency
- The spiral-wound cartridge offers simplified installation, convenient replacement, and clean, easy disposal of the spent cartridge
- The Rapid Liquid Sampler (RLS) allows simple field use of solid phase extraction materials and techniques.

Standard, commercially-available components are used to incorporate the disks and cartridges into portable, compact system that can operate at flow rates up to 300 mL/min for the disks and from 1 to 50 gallons per minute for the cartridges. Membranes have been developed for the capture of cesium, technetium, strontium, radium, lead and cobalt. Ongoing technical developments include particles and membranes for other targets. Successful demonstrations and deployments of both the cartridge and field sampling technology have been conducted.

INTRODUCTION

Much of the radionuclide-containing wastes that were left behind from nuclear weapons production exist in aqueous form. Additional aqueous waste is continually being generated from groundwater remediation and decommissioning activities. Large volumes of contaminated water exist at various facilities which also include fuel storage and disassembly basins. Current treatment of this water varies from bulk removal of the contaminated water to chemical treatment within the storage facility.

With the uncertainty of the integrity of the storage facilities over time, a technology that can remove radioactive contamination from the water while minimizing secondary waste generation is essential to the success of the remediation of the liquid wastes. A technology that is cost effective and safe is needed to process wastewaters on location without undue handling. The technology must reduce targeted nuclides to near regulatory release limits and condition the water for direct release.

3M has developed, teaming with the Department of Energy's National Energy Technology Laboratory, a new technology for selective detection and removal of dissolved radioactive materials from liquids. This technology utilizes particle-loaded membranes fashioned into disks and cartridges, and is intended to provide a cost effective alternative to present methods of sampling/analyzing, and large scale decontamination. The 3M technology provides a novel particle package with multiple benefits.

TECHNOLOGY DESCRIPTION AND BENEFITS

Empore™ Membrane

Empore membranes are thin membranes (0.5 mm) consisting of small (10 – 30 microns) element-selective sorbent particles enmeshed in a stable, inert matrix of polytetrafluoroethylene fibrils. Typically, particle mass in the membrane is 90%. The sorbent particles are densely packed, resulting in a very efficient sorption of the target element when aqueous samples are processed. Since no adhesives or binders are used to hold the particles, the full chemical activity of the particles is retained.

WWL™ Membrane

A second type of membrane, WWL, is comprised of active particles, fibers, and a binder. The fibers are chemically inert and stable over a broad range of aqueous conditions (high and low pH). In addition, they are very stable in a radioactive field and so are not subject to deterioration over prolonged use in such an environment. This membrane is less expensive to manufacture than Empore. In addition it has more rapid flow characteristics and resists particulate plugging better. Applications for WWL membranes are in devices where multiple layers of membrane are used to achieve efficient separations.

Technology Benefits

Both types of membranes secure small particles in place without disrupting the chemical reactivity of the particle. A wide variety of chemistries found in small particles or chemistries that can be bonded to small particles can be utilized by this technology. Common problems found with columns of small particles, including channeling, wall effects, and high pressure drops, are eliminated with the membranes. Low pressure drop means that these membranes can attain higher flow rates.

EMPORE™ RAD DISKS AND RAPID LIQUID SAMPLERS

Empore Rad Disks are Empore membranes cut into 47 mm diameter circles. These disks contain particle chemistries that selectively adsorb strontium, radium, technetium, or cesium ions and thus the disks selectively separate target radioisotopes even in the presence of large concentrations of competing ions. Because of the specificity of the sorbent particles, radioisotopes of a different element simply pass through the disk and remain in the filtrate. The effective sorption results in high chemical recovery of the target radioisotope. Typically, Rad Disks are used with laboratory vacuum filtration apparatus to process a one-liter sample of water in 20 minutes or less. This processing often eliminates conventional wet chemistry sample preparation steps such as precipitating, filtering, purifying, eluting, or evaporating. Improved productivity, turnaround time, and laboratory throughput result. Reagent use and waste generation are minimized.

Empore Rapid Liquid Samplers (RLS) are molded polypropylene parts that contain an Empore Rad Disk. A scrim support is incorporated into the RLS so that it can withstand an inlet pressure up to 50 psi. The RLS has luer lock connectors so that it can easily and securely be connected to a pump system. With positive pressure, flow rates through the RLS of up to 300 mL/min can be attained while maintaining quantitative recovery of the target radioisotope. Investigation into several methods for field analysis using the RLS are ongoing.

REMEDIATION CARTRIDGES

Construction

Each remediation cartridge is fabricated from a WWL™ membrane by converting the membrane into a uniform sheet, combining it with a scrim material, and winding it onto a hollow, perforated core. The formed article is referred to as a spiral-wound cartridge. The ends are then capped – one closed, the other open – to form the final article. The direction of flow through the cartridge is designed to be from outside to in; water surrounds the cartridge in its housing, passes through the layers of membrane, through the perforated core, and then out of the open end. Removal of the target radionuclide takes place as water passes across the active particles in the membrane layers.

Remediation cartridges may be prepared in a number of different sizes; a typical cartridge designed to process liquid at 1 to 2 gallons per minute measures 3” in diameter by 10” in length, and contains approximately 450 square inches of membrane with from 150 to 250 grams of available active particle. Larger cartridges have been designed to handle increased flow rates; an experimental cartridge measuring 6” in diameter by 22” in length was used to process water at a flow rate exceeding 15 gallons per minute. Cartridge dimensions are predicated both on system requirements for flow and back pressure and industry standards for filter vessels and housings. For instance, the open ends of the cartridges are fitted with o-rings that adapt to one of two industry-standard receptacles for filters, designated as 222 and 226.

Operation

Remediation cartridges are deployed in a system that includes a pump to provide water flow, filter vessels for containment of the active cartridges, appropriate valves and gauges for controlling and monitoring flow and pressure, plumbing to direct influent and effluent streams, and utility carts/tables to carry the system components. Since the requirements for each application vary, there are a variety of systems that may be provided with the cartridges. The simplest system is an arrangement of vessels in series: water enters at one end and passes through a vessel (or series of vessels) containing prefilters for solids removal, and then through active cartridges for radionuclide removal, exiting the opposite end of the system. Vessels may contain single cartridges or a multiple of cartridges. This latter arrangement is referred to as a 'nested' system. More advanced systems allow for the redirection of flow through the active vessels so that cartridges can be replaced in a manner that provides maximum remediating efficiency. The combination of large, nested cartridges in a redirectable flow system provides high flow rate in a continuous operation mode.

Demonstrations/Deployments

The Selective Separations remediation cartridge technology is presently deployed at Brookhaven National Laboratory on Long Island, New York, and at Savannah River Site in Aiken, South Carolina. A recently concluded demonstration at Ashtabula, Ohio provided further operational and performance data supporting the technology's use in field and industrial applications. These deployment sites were identified with the help of the National Energy Technology Laboratory (NETL) and were selected based on the availability of supporting site personnel. In the case of Brookhaven, a request was made to purchase a system to remove strontium-90 from 4000 gallons of tank waste, which would otherwise have to be disposed of as bulk liquid.

Ashtabula, Ohio

The RMI Titanium plant in Ashtabula, Ohio, processed uranium for the United States government from 1962 to 1990. As a result of operations, uranium and technetium-99 leached into soil around the plant. The 3M system used at the RMI facility (since converted to environmental restoration operations) targeted Tc-99 in groundwater that was being pumped out of soil drains to strip out trichloroethylene (TCE). Processing at 10 gallons per minute, the 3M remediation cartridge system successfully reduced effluent levels of Tc-99 from as high as 8000 pCi/L to well below the EPA release limit of 900 pCi/L throughout the course of the demonstration. Operated intermittently over a six-month period, a total of 17,045 gallons of groundwater was processed.

The Ashtabula system consisted of a pump, prefilters, and three vessels for containing the active Tc-99 removal cartridges. Each of these vessels housed nine cartridges measuring 3" in diameter by 10" in length. Arranged in-series, process water passed sequentially through the vessels to provide maximum removal efficiency even as up-front cartridges became loaded with the target analyte. When analysis determined that cartridges had reached capacity for technetium uptake, they were replaced with new cartridges. A simple change in valves redirected the flow so that the newly introduced cartridges became last in the sequence, insuring a continuous operation at maximum removal efficiency.

Manpower requirements to operate and monitor the 3M system at Ashtabula were minimal in relation to the simultaneous handling of the TCE stripping operation. Because the cartridge remediation equipment was plumbed in-line with the solvent removal apparatus the additional workload amounted to only about one hour per day of operation. The majority of this time involved an operator taking samples and recording operational data, with occasional changeouts of cartridges.

Capital costs for the 3M technetium removal system demonstrated at Ashtabula were approximately $20,000 for hardware and installation. Operational costs, including labor, were approximately $2.65/gallon.

Brookhaven National Laboratory

3M provided an operating filter system and cartridges to clean up 4000 gallons of tank waste that was being stored on site at Brookhaven National Laboratory. The primary contaminant was Sr-90, in levels varying from 15 to 700 pCi/L. Using three cartridges in a series arrangement, effluent levels of strontium were kept at or below 2 pCi/L throughout the cleanup effort. The first cartridge would reach saturation after about 600 gallons were processed – cartridges were in fact replaced after each 400 gallons to provide a safety margin – while the second and third cartridges provided polishing of the final effluent. The system was set up so that as new cartridges were introduced the valves could be changed so that the new cartridge was last in the series. This rotating arrangement insured maximum cartridge efficiency while maintaining excellent recovery of strontium. Processing at about 1.5 gallons per minute, the 3M Selective Separations Cartridge System proved to be a viable, cost-competitive alternative to reverse osmosis, column separation, or off-site bulk liquid disposal. The equipment remains on site, available for further use as needed. BNL has since purchased a second, larger system for removal of Sr-90.

Savannah River Site

The 3M Selective Separations membrane technology was demonstrated at the R-Disassembly Basin in February 1997. Processing at 6 gallons per minute, over 55,000 gallons of basin water was pumped through a vessel containing six cesium-removal cartridges with no breakthrough of the radionuclide. A later demonstration begun in 2000 has treated over 2 million gallons of basin water for the removal of cesium.

2000-2001 Savannah River Site

A recent demonstration of the 3M technology at the SRS R-Basin was intended to show efficient, cost effective removal of radioactive cesium with attention to simplifying operating procedures of the system. It was the intended goal to show that the 3M technology affords a cost-competitive, reliable, easy-to-use remediation system that can be turned over to site personnel for continued operation following initial set-up and a brief training period. The system included cartridges, the complete, cart-mounted filter system, which includes a pump for processing at 25 gallons per minute, vessels for prefiltration and active cartridges, appropriate gauges and valves, and a spill-tray/water-shield to contain inadvertent water release. Figure 1 shows a schematic drawing of this system.

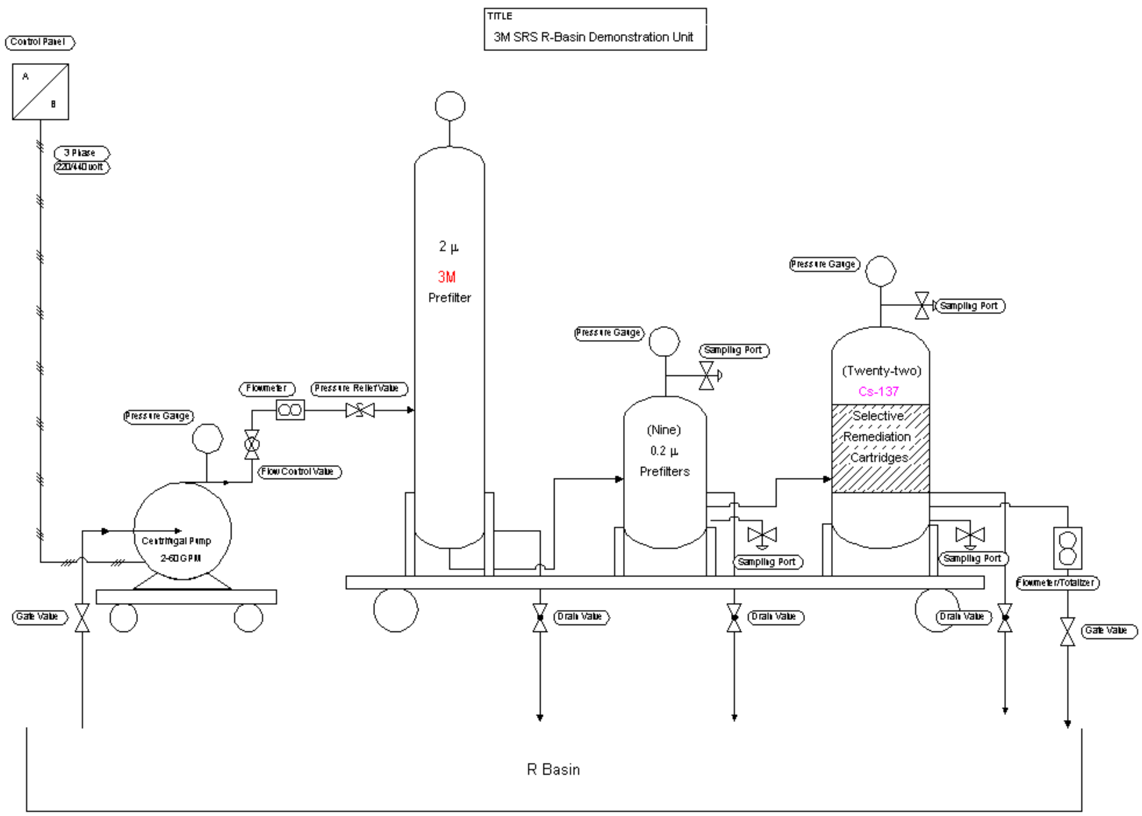

Fig. 1. 3M SRS R-Basin Demonstration Unit Schematic

The cesium removal demonstration is utilizing 22 active cartridges for capture of cesium-137 deployed in one vessel for active cartridges. Feed and effluent samples are being collected. Figure 2 shows the activity of these samples over the life of the project. Early results depict fairly high analytical detection limits. More refined techniques in later samples provided lower analytical detection limits. At the time of this writing (December, 2000) the system is still in operation. A total of two million gallons has been processed thus far. Removal efficiency for Cs-137 has been above 97% for the entire operation.

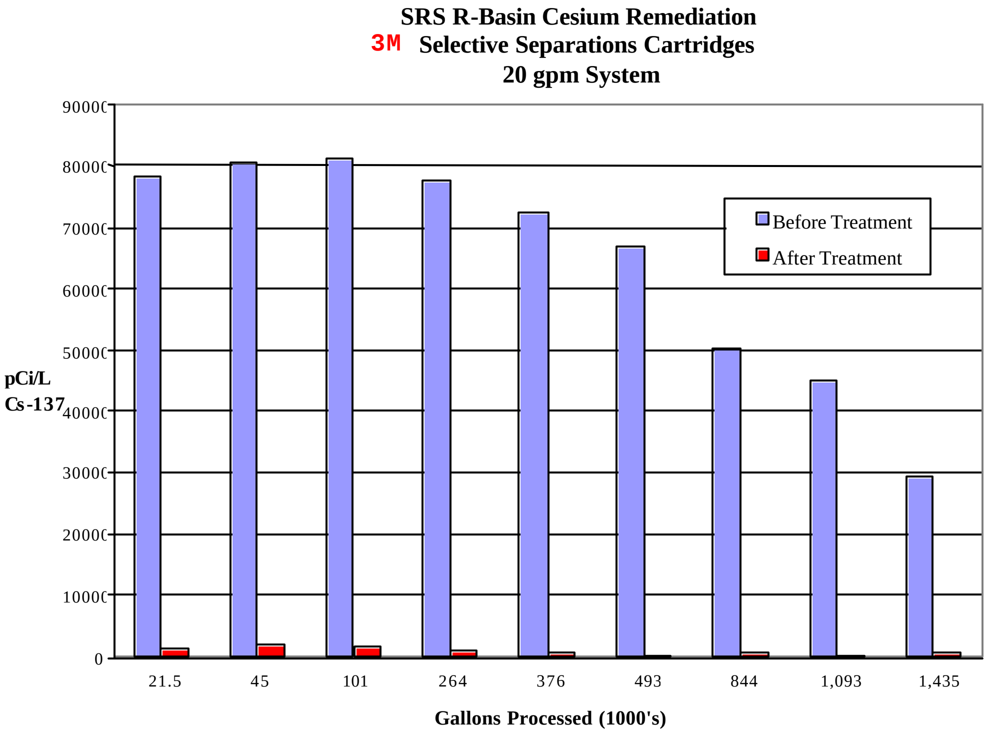

Fig. 2. 3M SRS R-Basin Cesium Remediation

In order to process large amounts of water through the active Cs-removal cartridges adequate prefiltration is essential. Figure 3 shows the build-up of pressure in the prefiltration units and their replacement. It also shows the unchanging, low pressure drop across the Cs-removal cartridges. These have not been changed. The initial 22 cartridges continue to perform well.

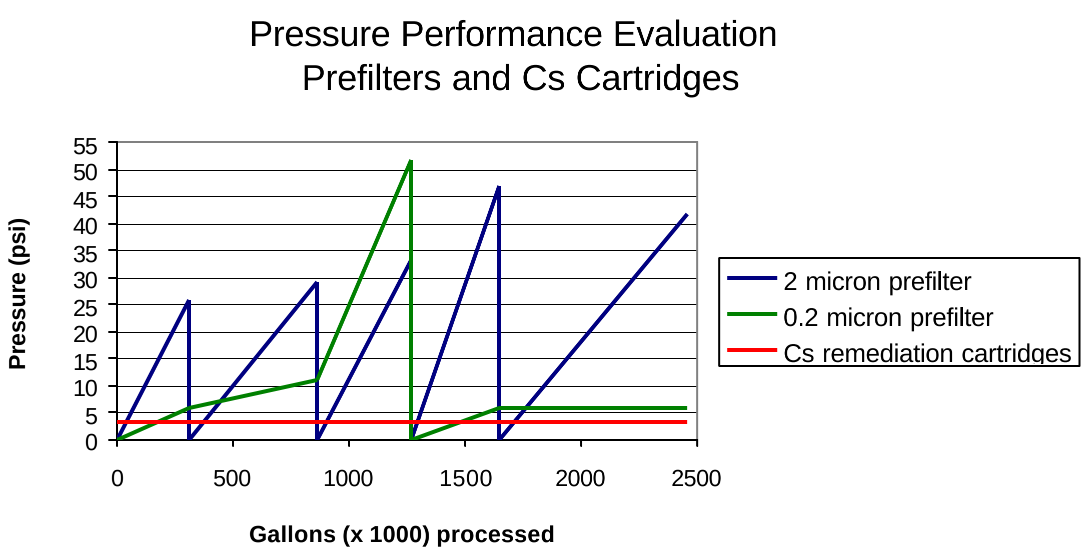

Fig. 3. 3M SRS R-Basin Pressure Performance

Multiple Remediation Cartridges Working Together

Most remediation sources do not contain a single contaminant. Therefore a remediation system must be easily adaptable for multiple contaminants. As part of the development of our membrane technology a series of tests to help determine the optimum arrangement of different kinds of remediation cartridges in a system have been conducted. Disk tests of cartridge membrane materials and subsequent single cartridge tests in aqueous matrices that contained multiple radioisotopes as well as matrix interference ions provided information on target and non-target adsorption. This information was used to build a laboratory system with five active small-scale remediation cartridges. A simulant matrix with four radioisotopes, lead and matrix interferences (primarily nitrate and calcium) was processed by the system. The nominal concentrations or activities were:

- Cs-137 160,000 pCi/L Pb 0.05 mg/L
- Co-60 45,000 pCi/L Ca 50 mg/L
- Tc-99 110,000 pCi/L NO_3 120 mg/L
- Sr-85 35,000 pCi/L Sr 0.12 mg/L

Figure 4 shows the results of this test. The cesium, cobalt, and technetium were completely retained. Lead was also retained well, although the graph reflects real variability in the concentration of lead in the challenge solution and an analytical detection limit too close to that concentration. Strontium did breakthrough during the course of this test since there was a significant concentration of calcium present. We are searching for a particle chemistry with improved selectivity for strontium over calcium at neutral pH. Nitrate was included since it can compete with Tc-99 removal. That was not a problem under the conditions of this test.

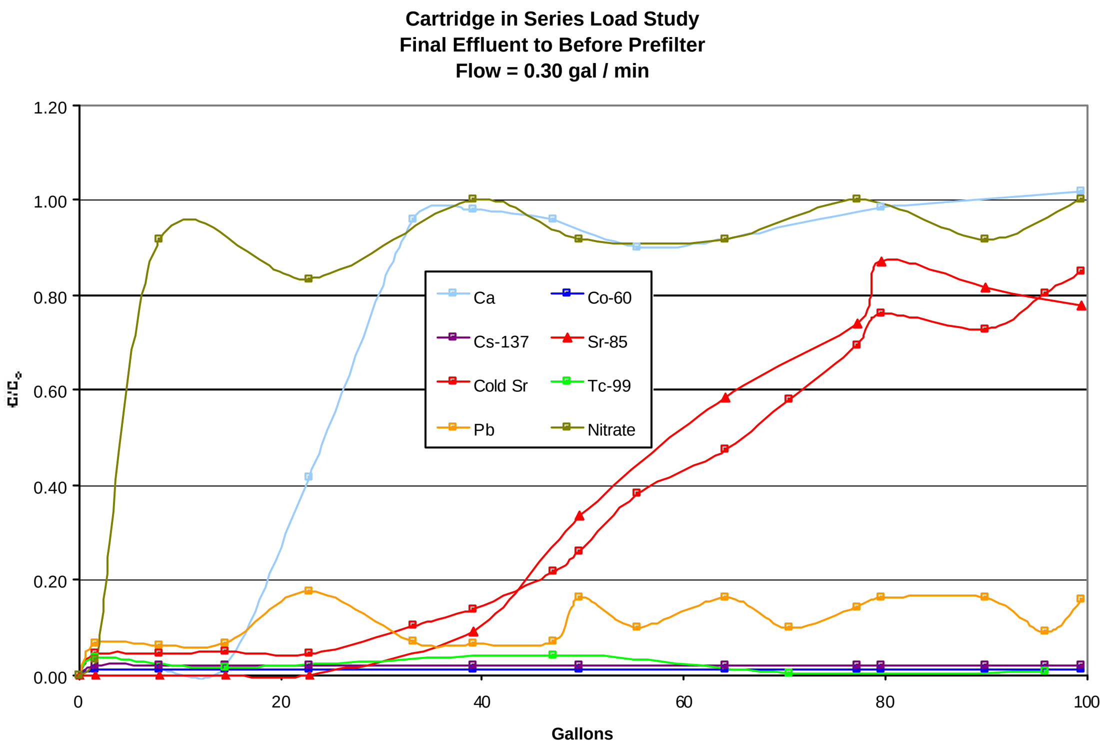

Fig. 4. Cartridge in Series Load Study Results

TECHNICAL RECOGNITION

Awards received for the technology developed under this program include:

* R&D Magazine's R&D 100 Award 1996
* Award for Excellence from the Federal Laboratory Consortium (FLC) 1997
* New Product Award from the American Filtration Separation Society (AFS) 1998
* R&D Millennium Top 40 1999

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