WATER AND WASTEWATER POLISHING USING 3M SELECTIVE SEPARATION REMEDIATION CARTRIDGE TECHNOLOGY

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ABSTRACT

3M has developed technology for selectively removing trace levels of dissolved contaminant materials from liquids using systems operating at flow rates up to 50 gallons per minute. This technology combines active particle chemistries with a particle-loaded membrane to achieve a new medium for liquid waste processing – a spiral wound filter cartridge. This technology has shown success by generating high decontamination factors and reducing contaminants to part per trillion levels.

The spiral wound cartridge offers simplified installation, convenient replacement, and clean, easy disposal of a concentrated waste. By incorporating small, high surface area particles (5 to 80 microns) into a sturdy, yet porous, membrane greater removal efficiencies of even trace contaminants can be achieved at higher flow rates than with conventional column systems. In addition, the captive-particle medium prevents channeling of liquids and insures uniform flow across the sorbing particle surface. The cartridges fit into standard, commercially-available housings and whole system capital costs are substantially lower than those of column or reverse osmosis systems.

Developmental work at high degrees of water polishing have included removal of mercury from contaminated wastewater, various radionuclides from process water, and organometallic species from surface water discharges. Laboratory testing and on-site demonstration data of these applications show the levels of success that have been achieved thus far.

Fig. 1. 3M Selective Separations cartridges

INTRODUCTION

The U.S. Department of Energy (under the guidance of the National Energy Technology Laboratory) has supported development of 3M's WWL™ membrane technology (a spin-off from 3M Empore™ technology) to address low level radiochemical contamination in a variety of large aqueous sources. Commercial needs / opportunities for removing low levels of non-radioactive dissolved metals have spurred a natural progression of this technology to investigating its use in many areas. These include government projects (primarily in the Department of Energy and Department of Defense areas), nuclear power plant pools and discharges, a variety of commercial and industrial process waters and wastewaters, and residential drinking water. The target chemical species that have been investigated thus far include radioisotopes of cesium, strontium, technetium, radium, uranium, cobalt, and antimony, and the metals lead, mercury, tributyltin, copper, and arsenic.

Cartridge Construction

The basic chemical action of a cartridge is dependant on the chemistry of the active particles within it. A variety of sorption chemistries are employed depending on the target chemical species and the chemical nature of the aqueous medium. All of the particles are very small (5 to 80 microns in diameter). The particles are formed into a membrane that typically has a final percentage of 65% (by mass) of the total membrane. The patented WWL™ membrane 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. The membrane has rapid flow characteristics and resists fine particulate plugging. Applications for membranes are in devices where multiple layers of membrane are used to achieve efficient separations.

WWL™ 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 than similar sized columns.

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 (as shown in Figure 2). 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.

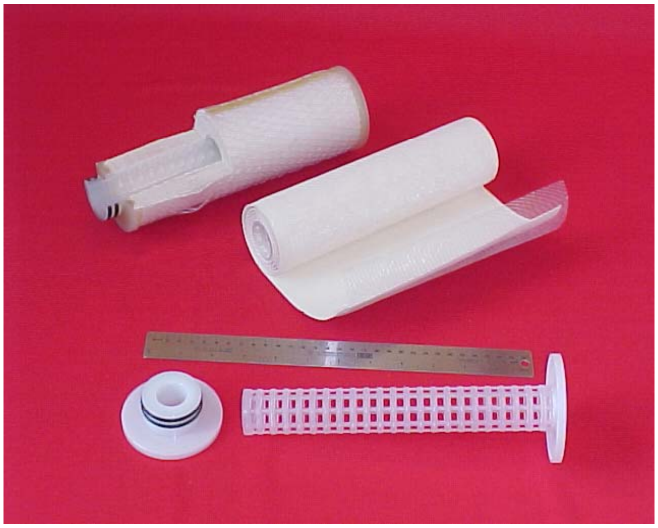

Fig. 2. Cartridge components and construction

Remediation cartridges may be prepared in a number of different sizes (as shown in Figure 1). A typical cartridge designed to process liquid at 1 to 2 gallons per minute measures 2.5" in diameter by 10" in length, and contains approximately 300 square inches of membrane with from 100 to 150 grams of available active particle. Smaller cartridges have been constructed for laboratory testing. Larger cartridges have been designed to handle increased flow rates. Cartridges measuring 6" in diameter by 22" in length have been used to process water at flow rates from 10 to 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. Flexibility in design and construction permits the use of other types of end caps as well.

Cartridge Operation

Remediation cartridges are deployed in a system that includes a pump to provide water flow, particulate filtration devices (if necessary), filter vessels for containment of the active Selective Separation 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 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. The micron size and loading capacity of the prefiltration devices will be dictated by the characteristics of the influent stream. Vessels may contain single or multiple 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.

New Challenges

In many areas of water and wastewater treatment, currently-used remediation technologies do not attain sufficient dissolved contaminant removal levels. Many of these extremely low levels are mandated by regulations or pending regulations. A few technologies may perform adequately but their cost is extravagant. These challenges can be met in several areas using WWL™ technology.

One of the benefits seen with the new WWL™ technology is the ability to remove target chemical species to extremely low levels – often to the ng/L (parts per trillion [ppt]) level or less. This capability, combined with the need to remediate water streams to extremely low levels, has led to testing the technology in several different test applications.

LABORATORY AND FIELD TESTS

In the following sections of this paper are summaries of laboratory and field tests where very low levels of contaminants have been treated by Selective Separations cartridges. Many other tests (primarily disk rather than cartridge tests) have been conducted while evaluating prospective particles and test membranes. The cartridge examples illustrate the successful high efficiency removal of target chemical species to levels often below analytical method detection limits. Also included are tests where cartridge performance has been evaluated with sufficiently sensitive analytical methods in order to assess its polishing performance. The decontamination factor (DF) is one measure of this polishing performance.

Decontamination Factor (DF)

This factor is the ratio of the concentration (or activity) of the target chemical species in the incoming stream to the concentration (or activity) in the processed solution (i.e., DF = [Influent]/[Effluent]). Decontamination factors generated under similar testing or operating conditions can be helpful comparison data. However, if they are generated from incoming concentrations that are exorbitantly higher than a real-life application they can be misleading. Also, in cases where the processed solution analysis is below the method detection limit, the decontamination factor will result in a greater than value. This value will only be as precise as the analytical method detection limit. Field analysis (or laboratories near field applications) often are not setup for lowest analytical detection limits possible. This often results in lower values for decontamination factors that are generated from field data compared to those generated from laboratory data.

Other test conditions can impact the measurement of a decontamination factor. Testing a simulated or naturally clean water (i.e., without customary chemical interferences) may produce a much higher decontamination factor. Performance improvement is usually seen when a series of cartridges are tested as opposed to a single cartridge. Slower flow rates may improve decontamination factors. Clearly the duration of a test, or how long a cartridge can attain a performance above a certain decontamination factor, is as important as the decontamination factor itself. An initial decontamination factor may be outstanding but if it degrades quickly during use of the cartridge then the cartridge is of very limited value. This value, along with other cost-related items (e.g., initial capital cost, operation and maintenance costs), must be evaluated and compared for various remediation technologies.

Technetium

The first entry in Table I summarizes a laboratory study using two 2.5" diameter by 3" long technetium removal cartridges in series. A total of 190 gallons of wastewater simulant was treated. The first 120 gallons of this treatment produced a concentration of technetium in the final effluent of <5 parts per trillion (ng/L). The influent (or feed) concentration averages 1400 parts per trillion (1.4 parts per billion). These data lead to a calculated decontamination factor of greater than 280.

Table I. Technetium (Tc) Test Results

Test Description	Influent	Effluent	DF
Laboratory study	24000 pCi/L (1.4 ppb)	<85 pCi/L (<5 ppt)	>280
Soil remediation wastewater	2700 pCi/L (160 ppt)	2 pCi/L (0.12 ppt)	1350

The second entry in Table I is the removal of technetium from wastewater generated from a soil remediation operation. Here three vessels of cartridges were run in series. Each vessel had nine 3" diameter by 10" long technetium removal cartridges. The flow rate through this system varied from five to ten gallons per minute. About 5000 gallons were processed up to the point reported in the table. Earlier measurements showed less than 1 pCi/L being discharged and corresponding decontamination factors of 2000 to 4000. Low pCi/L analytical results were achieved using 3M Empore™ Technetium Rad Disks and processing sample volumes of one to four liters. With replacement cartridges, a total of 17,000 gallons was processed during this operation. Since the treatment goal was only 900 pCi Tc-99/L high efficiency did not need to be maintained. Overall, no system effluent activities were greater than 500 pCi/L and most were less than 50 pCi/L.

Cobalt

Trace cobalt contamination is a concern in nuclear power generation and nuclear materials processing. Cobalt and copper show similar chemical behavior. A site for the demonstration of a high flow test was not available for cobalt so a copper site was chosen.

The laboratory study for cobalt used a 2.5" diameter by 3" long cartridge to process 100 gallons of simulated groundwater. The detection limit of the effluent analysis was limited by the sensitivity of the gamma spectroscopy measurement and the presence of other radionuclides in the simulant.

Table II. Cobalt (Co) / Copper (Cu) Test Results

Test Description	Influent	Effluent	DF
Co-60 laboratory study	45000 pCi/L	<1000 pCi/L	>45
50 gpm system treating Cu in plating wastewater	22 ppm	0.11 ppm	200

The 50 gallon per minute copper removal demonstration used seven 6" diameter by 20" long cartridges in one vessel. The influent concentration varied from 20 to 25 parts per million (mg/L) during this test. This level is much higher than other tests in this paper. Since the treatment system had only one vessel of cartridges the benefits of a series of cartridge treatments were not realized. Approximately 2700 gallons were treated at the performance level shown in the Table II. The overall test processed about 12,000 gallons before full saturation of the cartridges had occurred.

Tributyltin

Table III. Tributyltin (TBT) Test Results

Test Description	Influent	Effluent	DF
Laboratory single cartridge testing	1200 ppb	500 ppt	2400
Hull wash water on-site test	100 ppb	<10 ppt	>10,000

A laboratory cartridge test using a single 2.5" diameter by 7" long cartridge to remove TBT from a brackish water simulant processed 1000 gallons as shown in Table III. The 500 ppt effluent concentration reported was the maximum TBT effluent seen during these 1000 gallons. Most concentrations were less than 100 ppt.

The hull wash water test was conducted on-site. Pending surface water discharge regulations require less than 50 parts per trillion (ng/L) TBT in the effluent. This test used three single cartridges in series to treat about 5000 gallons at approximately one gallon per minute flow rate.

Mercury

Remediation requirements for mercury involve reducing concentrations from the part per billion (ug/L) range to low part per trillion (ng/L) levels. To evaluate these low concentrations a special Environmental Protection Agency test method (EPA Method 1631, gold amalgam – atomic fluorescence spectrophotometry) was used.

Table IV. Mercury (Hg) Test Results

Test Description	Influent	Effluent	DF
Laboratory simulant cartridge series test	40 ppb	1 ppb	40
Laboratory test on process water sample	2500 ppt	10 ppt	250
20 gpm field test	4000 ppt	<100 ppt	>40

The first mercury test in Table IV shows results from a test using laboratory simulant water. Here a series of three 2.5' diameter by 3" test cartridges were used to treat about 500 gallons of water. Figure 3 shows how the first cartridge in this test removed mercury until it began to breakthrough while the second and third cartridges continued to provide a clean effluent.

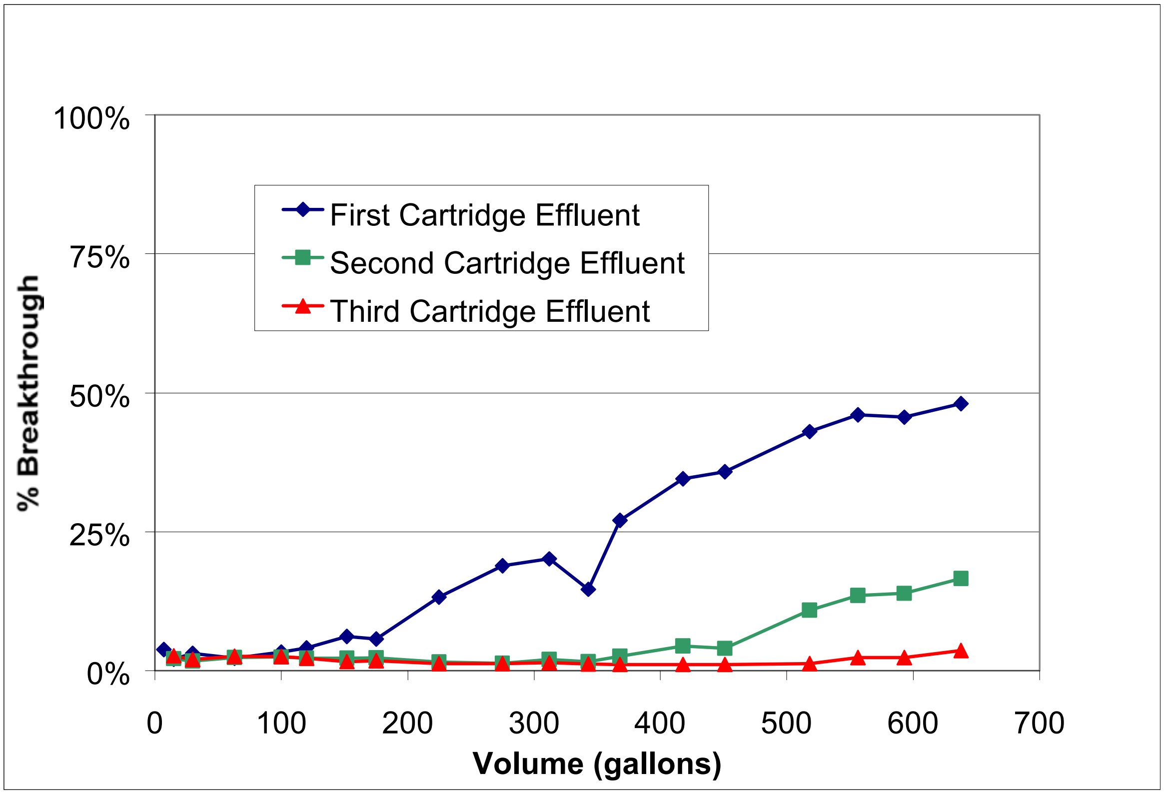

Fig. 3. Mercury cartridge series breakthrough curve

The second mercury test listed in Table IV took a sample of 16 gallons of actual process wastewater and tested it through a single 2.5" diameter by 3" long cartridge. At a flow rate of 0.25 gallons per minute the influent mercury concentration (after prefiltration) of 2500 parts per trillion was reduced to less than 10 parts per trillion.

The third test results are from an industrial field test using seven 2½" diameter by 20" long cartridges. This test ran at approximately 20 gallons per minute and treated over one million gallons.

Cesium

Table V includes the summaries of three cartridge remediation activities involving the removal of cesium. In these studies the amount of one particular radioisotope of cesium (cesium-137) is reported. Other cesium isotopes (either radioactive or stable) that were present were not quantified. Detection limits of the effluent analyses were limited by the sensitivity of the gamma spectroscopy measurements and by the presence of other radionuclides in the simulant.

The first laboratory study for cesium used a 2.5" diameter by 3" long cartridge to process 100 gallons of simulated groundwater.

The second laboratory study for cesium also used a 2.5" diameter by 3" long cartridge. This study processed 50 gallons of basin simulant water at approximately 0.25 gallons per minute with no detectable cesium-137 breakthrough. The lower detection limit on this effluent sample was achieved by using longer analytical counting time.

Table V. Cesium (Cs) Test Results

Test Description	Influent	Effluent	DF
100 gallon laboratory test	150 nCi/L (1.7 ppt)	<1 nCi/L (<0.01 ppt)	>150
Fuel basin water simulant laboratory test	81 nCi/L (0.97 ppt)	<0.2 nCi/L (<0.002 ppt)	>400
Fuel disassembly basin water demonstration	81 to 12 nCi/L	0.80 to <0.07 nCi/L	36 to 560

The third example cited in Table V is the treatment of 6.8 million gallons of fuel disassembly basin water that was treated by a single vessel containing twenty-two 2.5" diameter by 22" long cesium removal cartridges. This system operated at 10 to 20 gallons per minute in a recirculating mode over 15 months of operation. Figure 4 shows the test results of both influent and effluent samples throughout the treatment process. The first five effluent results show very high detection limits. Later results were generated using a more sensitive analytical technique with a lower detection limit. The overall decrease of the influent activity shows the cleanup effects on the basin contents.

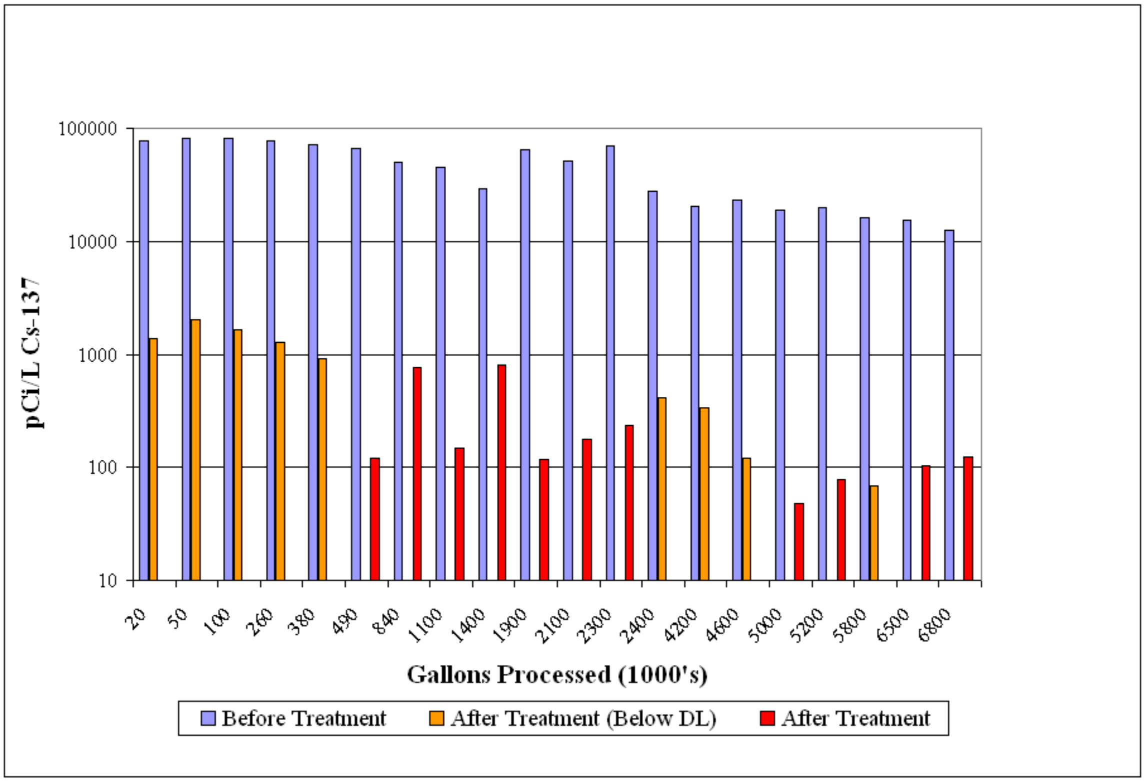

Fig. 4. Cesium removal from fuel basin water

SUMMARY

A variety of laboratory and field tests have been conducted using 3M Selective Separation Remediation Cartridge technology. Many of these tests have demonstrated the polishing performance of the technology. Decontamination factors in the hundreds or even thousands have been attained and often contamination concentrations have been successfully reduced to part per trillion (ng/L) levels or less. Future testing and remediation applications will include nuclear power plant and other industrial process and wastewater sites.

ACKNOWLEDGEMENTS

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