

## **DEVELOPMENT OF COMPOSITE FILTERS FOR SELECTIVE REMOVAL OF RADIONUCLIDES**

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### **ABSTRACT**

Development, testing, and successful deployment of granular inorganic ion selective media have been well documented. These media currently are used to treat radioactive waste from nuclear power plants, nuclear fuel reprocessing plants, nuclear facilities undergoing decontamination and decommissioning, and contaminated ground waters. These materials do require ample retention time to achieve superior kinetics, however. In the United States, most nuclear plant radwaste systems currently utilize relatively large diameter vessels that do not allow proper flow paths to optimize kinetics of selective media. Graver Technologies developed finely divided Ecodex<sup>®</sup> CsFloc, Ecodex<sup>®</sup> CoFloc and Ecodex<sup>®</sup> SrFloc media with increased surface area and improved kinetics to overcome this problem. Laboratory testing, including evaluations in the Radiochemistry Laboratory of the University of Helsinki, of these media have confirmed their efficacy in terms of selective radionuclide removal. Using nuclear power plant simulated floor drain waters containing <sup>134</sup>Cs or <sup>57</sup>Co radionuclides, the CsFloc and CoFloc media offered selective radionuclide removal combined with a long throughputs. In these experiments the selective media were precoated onto filter elements; however, many nuclear plants do not have the proper equipment (precoat systems) currently installed for this application. Consequently, Graver Technologies developed a composite filter that contains ion selective media sandwiched between two flat filters. These novel composite filters combine filtration and ion exchange / adsorption unit processes within a single cartridge. These cartridges can be tailor-made for specific applications. Moreover, they are fully compatible with current systems in that they can be used in existing cartridge housings without modification. Various prototypes of these composite filters have been designed and constructed. Two such prototypes (one filled with CsFloc media and one filled with CoFloc media) were constructed for alpha site testing at the TXU Comanche Peak Steam Electric Station radwaste facility. These cartridges were tested using a slipstream from the radwaste system operated by Duratek, Inc. at this plant. The CsFloc composite filter was under test from early 2003 until the fall 2003 outage at Comanche Peak. Testing of the CoFloc composite filter began during that outage. Preliminary results from the CsFloc composite filter test appear quite promising.

## INTRODUCTION

Both filtration and ion exchange have been used in nuclear power plants since the first of these plants began commercial operation more than forty years ago. Both of these unit processes appear in various operations common to nuclear plants. Examples of these applications include make-up demineralization, condensate polishing, radwaste treatment, and blowdown demineralization. Typically, in these applications ion exchange resins are utilized either in deep beds of resin beads or shallow precoats of powdered resin. A wide variety of filters are used in many locations throughout a nuclear power plant and for many specific functions. Although deep beds of ion exchange resins provide rough filtration, complete removal of suspended solids, such as the colloidal forms of iron or cobalt, generally require separate filtration vessels. Since powdered resins are applied onto septa or filter elements, they combine the ion exchange and filtration functions in a single vessel. Moreover, many precoats contain fibers or other components that further improve filtration. The composite filters discussed in this paper carry this idea of combining ion exchange / adsorption and filtration functions, albeit in a different format.

Ion exchange resins have been used to treat waste streams, including radwaste generated by nuclear power plants, for many years. Originally, standard synthetic organic ion exchangers, such as strongly acidic cation resins and strongly basic anion resins, alone or in combination in a mixed bed, were chosen for this service. As the need to remove particularly troublesome (i.e., extremely prevalent or long half-life) radionuclides grew, more specific organic resins were developed for this purpose. At the same time, researchers began evaluating inorganic ion exchange resins, commonly known as zeolites, for this application [1]. After years of development, numerous synthetic and natural inorganic ion exchange resins are currently available for treating radwaste. The most efficient inorganic exchangers (e.g., titanates [2], silicotitanates [3-5], and hexacyanoferrates [6-9]) can remove radionuclides selectively even from concentrated radwaste solutions. In addition to higher selectivity, these inorganic ion exchangers offer better radiation stability in the treatment of nuclear waste effluents.

As noted above, ion exchange applications traditionally utilized columnar operation with granular or bead form particles. The rate of exchange of ionic species is controlled by mass transfer kinetics through the fluid surrounding the particle and through the particle itself. For inorganic materials, the rate of ion diffusion (commonly called kinetics) is relatively low, even more so than for standard organic ion exchangers. Powdered organic ion exchange resins have been used in precoat demineralizer applications (the so-called Powdex<sup>®</sup> process [10]) in condensate polishing and waste treatment applications in nuclear power plants for many years. These powdered resins provide better kinetics than their granular counterparts since the particles of the powder are inherently smaller than those for the bead. Thus, finely divided powders of the inorganic ion exchangers offer an attractive alternative for improving exchange kinetics without sacrificing removal efficiency. Decontamination factor or “DF” is defined as the ratio of the feed activity divided by the effluent activity as shown in Equation 1.

$$DF = \alpha_{\text{feed}} / \alpha_{\text{effluent}}, \quad (\text{Eq. 1})$$

Ideally, the DF should remain virtually constant over a wide range of flow rates for a kinetically insensitive material. Conversely, the DF will drop as the flow rate increases for a kinetically sensitive material.

## BACKGROUND

The Louviisa Nuclear Power Plant in Finland first used CsTreat<sup>®</sup>, a hexacyanoferrate-based granular material made by Selion Oy<sup>α</sup>, in 1991 for purification of evaporator concentrates [9]. Granular CoTreat<sup>®</sup>, a titanium oxide based material, was subsequently introduced and has been used by a number of nuclear power plants and nuclear facilities [11]. Utilizing proprietary technology, the Research and Development staff at Graver Technologies developed a class of novel finely divided media based on the same chemistry. Each individual material selectively removes ions of a specific element or elements from a multi-component feed stream.

Three specific powdered media were developed for treatment of nuclear plant radwaste. Each material selectively removes ions which have proved difficult to eliminate by more traditional means. The media designated Ecodex<sup>®</sup> CsFloc GL-750 is highly selective for cesium ions such as <sup>134</sup>Cs and <sup>137</sup>Cs. The CsFloc also exhibits selectivity for <sup>58</sup>Co and <sup>60</sup>Co. Similarly, the media designated Ecodex<sup>®</sup> CoFloc GL-792 is highly selective for cobalt ions such as <sup>58</sup>Co and <sup>60</sup>Co, while offering some selectivity for manganese (<sup>59</sup>Mn), iron (<sup>59</sup>Fe), zinc (<sup>65</sup>Zn), and plutonium (<sup>240</sup>Pu). The media designated Ecodex<sup>®</sup> SrFloc GL-760 is selective for strontium ions such as <sup>85</sup>Sr and <sup>90</sup>Sr. All of these media can be incorporated into a composite filter.

These selective media consist of flocculated particles similar to traditional ion exchange precoats. Thus, they can be used in traditional precoat applications and are compatible with various filter and septum configurations. In the composite filter, these media are combined with conventional wrapped flat filter media to allow both particulate filtration and selective ion exchange.

## EXPERIMENTAL

### Media Characterization of Novel Precoat Materials

The selective media have been characterized in the Graver Technologies Laboratories at Glasgow, Delaware and Newark, New Jersey [12,13]. Due to their finely divided nature, important properties include particle size distributions and hydraulic considerations (flow and pressure drop). Particle size distributions were determined using a Coulter LS 230 Particle Size Analyzer commonly used to measure both ion exchange bead and powder particle size distributions. This equipment allows measurements from 0.04 μm up to 2000 μm. Mean sizes of 110 μm for CsFloc and 76 μm for CoFloc were measured for the media used in the alpha site trials discussed below. These values are typical for conventional powdered ion exchange precoats.

Hydraulic performance including pressure drop as a function of flow rate and permeability for liquids is a key property for precoats. A series of trials was run on a prototype selective resin precoat to measure pressure drop as a function of bed depth. These tests were conducted in glass

columns with fritted disk supports rather than with precoated filters or septa. Table I summarizes this data for bed depths of 2.5 to 11.7 cm (1.0 to 4.6 in) and flow rates of 2.44 to 24.4 L/h (1 gpm/ft<sup>2</sup> to 10 gpm/ft<sup>2</sup>). As expected, pressure drop across the precoat bed remains relatively low for all bed depths tested with relatively low flow rates. However at the 24.4 L/h flow rate, pressure drop increases relatively rapidly as bed depth is increased and exceeds 207 kPa (30 psi) beyond the 10 cm bed depth.

Table I Hydraulics of Selective Resin Precoat as a Function of Bed Depth

Flow Rate (L/hr)	→	2.44	4.88	9.76	19.52	24.40
		Pressure Drop (kg/cm <sup>2</sup> )				
		↓	↓	↓	↓	↓
Bed Depth (cm)						
↓						
2.54		0.021	0.084	0.169	0.457	0.555
3.61		0.021	0.098	0.267	0.647	0.858
5.08		0.070	0.197	0.387	0.844	1.12
5.89		0.169	0.225	0.366		
7.62		0.141	0.295	0.619	1.34	1.71
9.75		0.162	0.352	0.759	1.57	1.90
11.73		0.211	0.464	0.928	1.93	2.44

### Radionuclide Decontamination Trials Using Novel Precoat Materials

Since Graver Technologies does not have a license to work with radioactive materials, actual radionuclide decontamination trials were conducted at the University of Helsinki, Laboratory of Radiochemistry, Department of Chemistry under the direction of Professor Risto Harjula. Dr. Harjula and his research group are well known for their work with inorganic ion exchangers, especially those associated with hexacyanoferrate and titanium oxide chemistries [14,15].

Dr. Harjula evaluated both the CsFloc and the CoFloc media using a bench top Single Element Precoat Pilot Plant [16] built by Graver Technologies. This pilot plant consists of a 25.4 cm (10 in) wound yarn precoat filter element, a slurry tank, a precoat pump with auxiliary piping, and appropriate meters and valves. The selective media were precoated onto the filter element with recirculation in the traditional manner. Both media were pretreated via soaking in a dilute salt solution as proscribed by the manufacturer. Two types of simulated floor drain (FD) waters were utilized during the testing: the first (FDA) represented a medium-salt floor drain contaminated with radiocesium; the second (FDB) simulated a low-salt floor drain contaminated with radiocobalt (see Table II).

Table II. Chemical Composition of Simulated Radioactive Waste Solutions

<u>Constituent</u>		<u>FDA</u>	<u>FDB</u>
Na (ppm)		204	43
K (ppm)		19	17
Mg (ppm)		12	0
Ca (ppm)		40	0.5
NO <sub>3</sub> (ppm)		560	106
pH		6.9	6.8
<sup>134</sup> Cs (Bq/L)		50 - 70	0
<sup>57</sup> Co (Bq/L)		0	50 - 70

A second pump circulated the simulated floor drain waste water through the precoat filter element from a 60 L (15.85 gal) external feed tank. Concentrated solutions of radionuclides (either <sup>134</sup>Cs or <sup>57</sup>Co) were fed continuously into the feed tank to maintain the feed level in the 50 to 70 Bq/L range. The flow rate of 210 – 240 L/h (0.925-1.057 gpm) through the filter element corresponds to 1500 – 2200 BV/hr. Radionuclide activity concentration was determined from periodic samples taken on the outlet side of the precoat filter.

Performance of powdered CsTreat and CsFloc media were compared using the pilot plant described above. Figure 1 illustrates the DF's obtained as a function of throughput volume. In this trial, the precoat dosage of 100 g for CsTreat and 80 g for the CsFloc, a flow rate of 4 L/min (1.057 gpm), and the FDA feed with <sup>134</sup>Cs as the radionuclide in the feed. The CsFloc produced a high DF (>60) up to 90,000 L/kg at which point the trial was terminated on time constraints. No increase in differential pressure ( $\Delta P$ ) was observed throughout the run. Figure 2 illustrates a similar trial comparing powdered CoTreat and CoFloc. In this trial, the FDB feed water with <sup>57</sup>Co as the radionuclide was used instead of the FDA feed water. The CoFloc produced a DF between 3 and 6 up to 500,000 L/kg when the test was terminated. It should be noted that this modest DF for <sup>57</sup>Co increased dramatically when the feed activity was increased to 1000 Bq/L or higher. Although not illustrated in Figures 1 and 2, a standard powdered strongly acidic cation resin (Powdex<sup>®</sup> PCH) was also included in these trials. The DF for PCH never exceeded 2 for either trial.

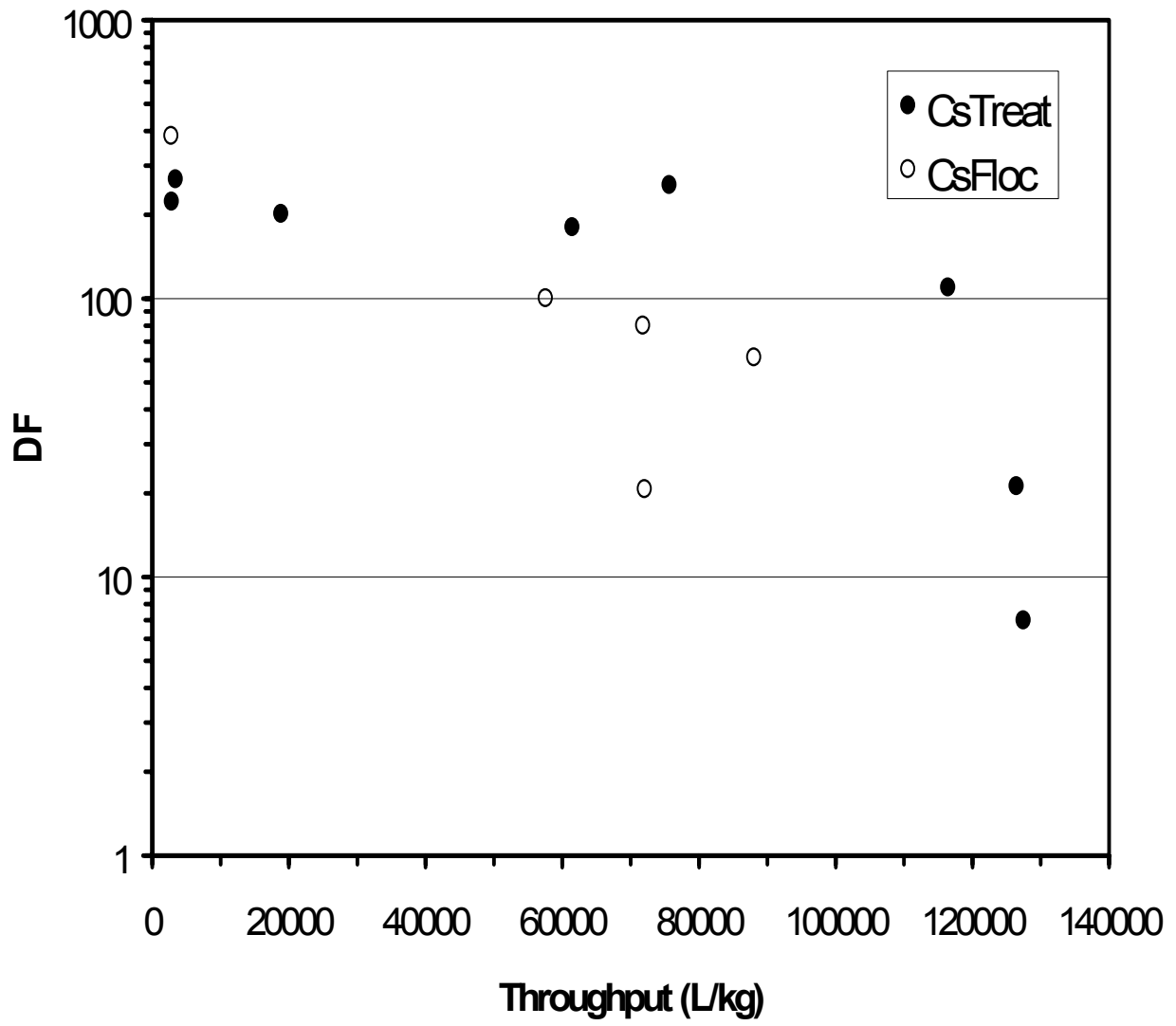


Fig. 1 Decontamination Factor for Cesium Selective Media

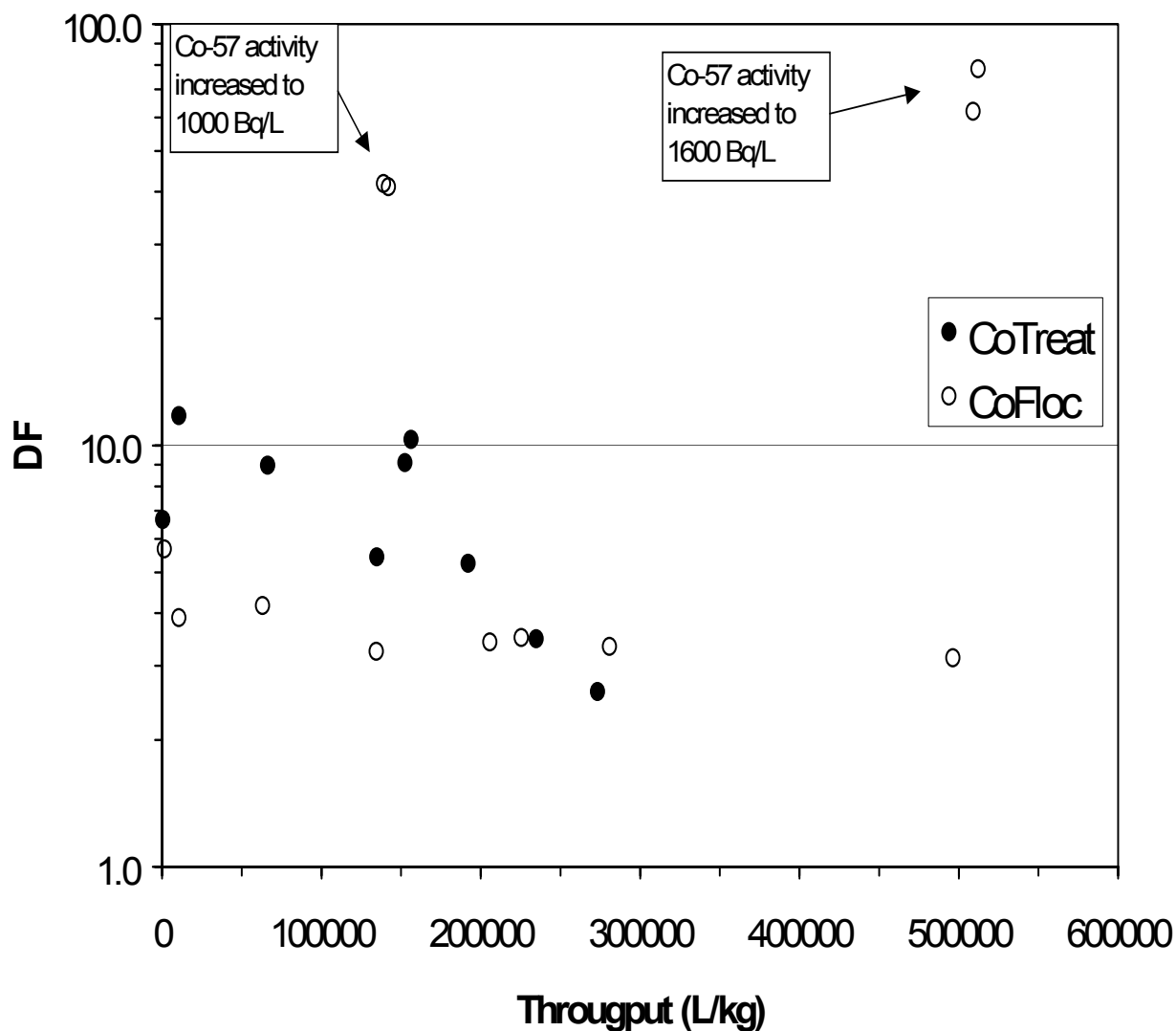


Fig. 2 Decontamination Factor for Cobalt Selective Media

Dr. Harjula also conducted a study on the effect of feed activity on the performance of the precoat. In addition to the two novel selective media (CsFloc and CoFloc), the PCH and a powdered weakly acidic cation (coded as GX089) resin were included as controls in this study. Figure 3 summarizes these results. For the CsFloc and the CoFloc the DF increased linearly as a function of feed activity when plotted on a log / log scale. By contrast, the DF's for the two conventional organic resins remained low and unaffected regardless of feed activity. Consequently, the kinetic mechanism of radionuclide uptake is strikingly different for these two types of media.

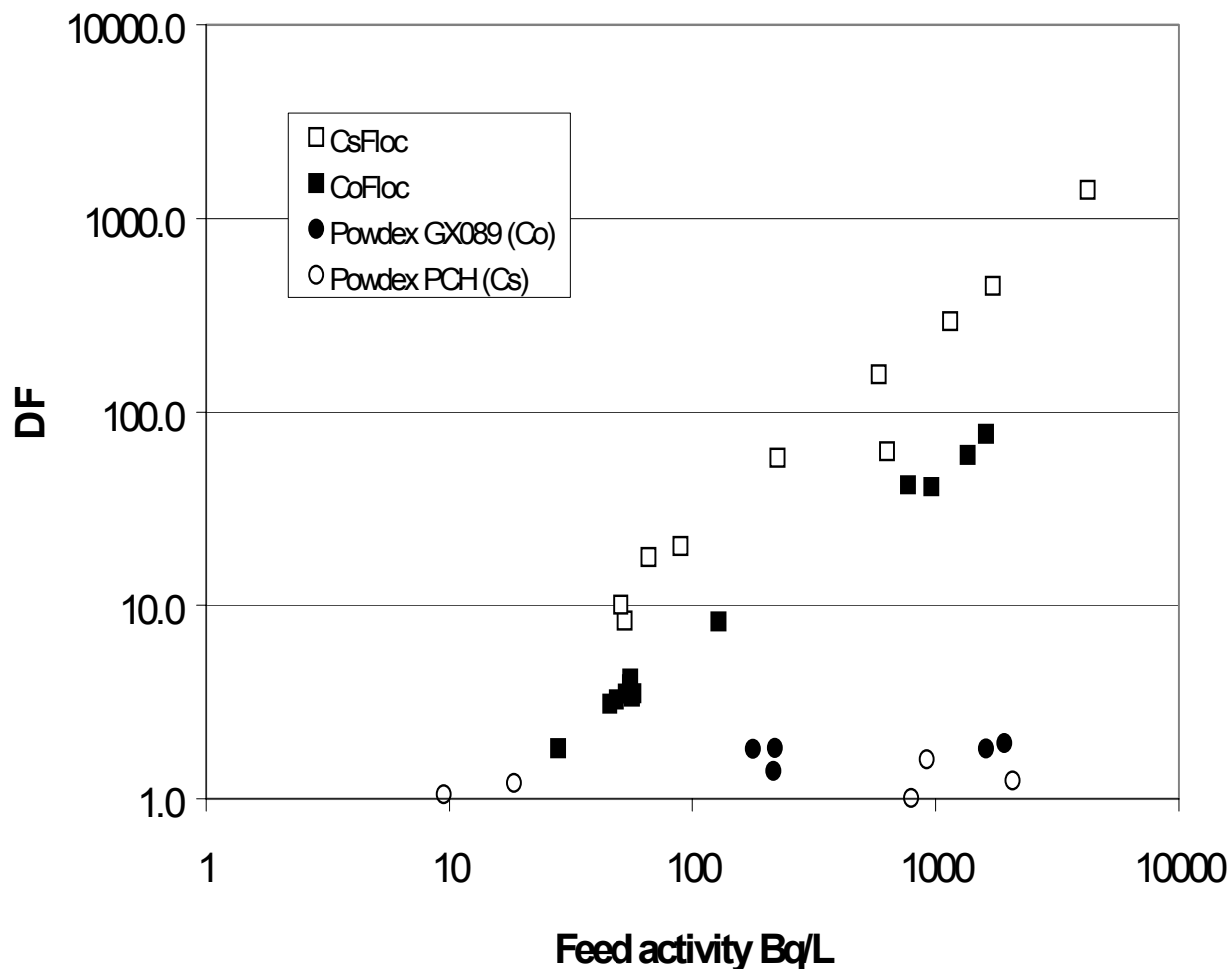


Fig. 3 Decontamination factor as a function of feed activity

### Composite Filter Development

Novel composite filters have been developed that utilize the selective media described above. A number of prototypes have been assembled at the behest of specific customers. The first prototype composite filters were cartridges with dimensions of 15.2 cm (6 in) in diameter by 48.3 cm (19 in) in height. The components of the filters included a stainless steel support cage, an external filter sleeve, an annulus packed with the CsFloc media, an internal filter sleeve, and a stainless steel support tube. The external and internal filter sleeves both consisted of double wraps of flat filter media rated at 40  $\mu\text{m}$ . Feed liquid enters through the inside filter wraps, flows radially across the media annulus, and exits through the outside filter wraps. It should be noted that the novel precoat media used is suitable for the short ion exchange zone necessitated by this



design. These filters were designed to fit into existing filter housings at the South Texas Project (STP) nuclear plant. Their primary purpose was to selectively remove cesium ions from the radwaste at this plant immediately prior to discharge. Since these composite filters would be installed in lieu of existing filters, the flat filters surrounding the annulus of cesium selective media were selected to meet specific filtration criteria. To date these composite filters have not been evaluated at this plant. One positive aspect of this delay is that the composite filters do not have shelf-life limitations like many conventional organic media.

The Comanche Peak Steam Electric Station (SES), a two unit PWR nuclear plant operated by TXU, expressed interest in testing a composite filter capable of selectively removing trace quantities of radioactive cesium from the liquid radwaste system at this plant. As originally envisioned, the composite filter would act as the final polishing unit prior to discharge to the environment. Specifically, influent activity levels of cesium needed to be reduced below the limit of detection of approximately  $5\text{E-}8 \mu\text{Ci/L}$  prior to discharge. Typically, this reduction required DF's of 10 to 100. The actual filter design went through a series of iterations prior to actual fabrication at Graver Technologies. The final design utilized a 6.0 cm (2.375 in) diameter by 25.4 cm (10.0 in) length filters with a nominal 1.3 cm (0.5 in) inner annulus of selective media. As with the initial STP prototypes discussed above, the inner and outer filter sleeves consisted of double wraps of flat filter media rated at  $40 \mu\text{m}$ . Two prototype filters were fabricated: one containing CsFloc media and one containing CoFloc media.

Comanche Peak SES personnel undertook preliminary trials with CsTreat, CoTreat, CoFloc, and several media controls prior to installing either composite filter<sup>β</sup>. The CsTreat media outperformed all other candidates in terms of both cesium and cobalt removal from radwaste. With this encouraging data in hand, the prototype composite filter containing CsFloc was finally installed in the radwaste system at Comanche Peak SES in late February 2003. The composite filter was installed in a slipstream from the ALPS<sup>®</sup> radwaste system operated by Duratek at the Comanche Peak plant, as opposed to the final polisher position originally envisioned. Figure 4 is a schematic diagram of this filter demineralizer system used to process radwaste at Comanche Peak SES. It should be noted that Vessels 5 & 6 in this system contain proprietary selective media supplied by Duratek, Inc. The slipstream feed for the composite filter trials was taken from the effluent side of the initial carbon bed (Vessel 1 in Figure 4) and the effluent from the composite filter was directed to a floor drain. The actual test was run intermittently over a period of approximately 8 months until the fall 2003 outage at this plant. A total of 8,384 L (2,215 gal) of radwaste was processed through the composite during this trial. A flow rate of 227L/hr was maintained throughout the test. Initially, the differential pressure across the filter was 103 kPa (15 psi); by the end of the test the differential pressure had risen to 309 kPa (45 psi) and the flow rate of 227 L/hr could no longer be maintained. At the end of the trial, an autopsy was performed on the composite filter to determine isotopic loading. Table III summarizes the results of that autopsy. The total Curie loading on the filter was  $2.67 \mu\text{Ci}$  while the contact exposure level was 5 mr/hr. This composite filter was most effective for cesium removal (56.3% of the measured activity came from cesium isotopes), though both cobalt and manganese isotopes were also removed. Beyond the five isotopes listed in Table III, activity from other isotopes represented only 3.5% of the total loading. Influent and effluent activity measurements were taken during each processing session. This data was not available when this paper was written, however.

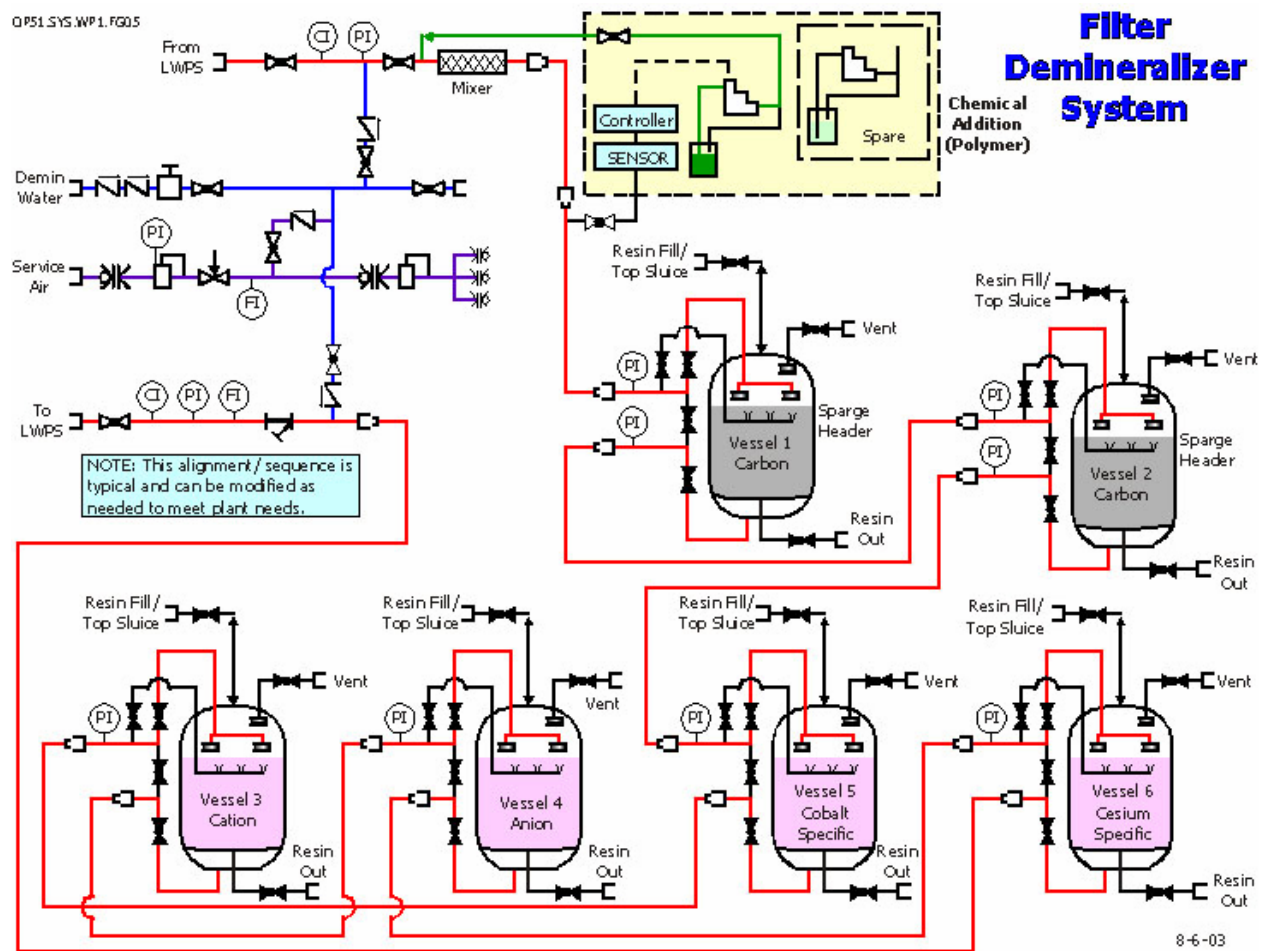


Fig. 4 Schematic diagram of filter demineralizer system for Radwaste processing<sup>7</sup>

Table III Isotopic Analysis of CsFloc Composite Filter

<u>Radionuclide</u>	<u>Activity</u>	<u>Activity Percentage</u>
<sup>54</sup> Mn	0.414	15.5%
<sup>58</sup> Co	0.152	5.75
<sup>60</sup> Co	0.476	17.8%
<sup>134</sup> Cs	0.504	18.9%
<sup>137</sup> Cs	1.030	38.6%

## CONCLUSIONS

Results to date have been very promising for the composite filters containing novel precoat. In laboratory testing, these precoat exhibit excellent removal of the targeted dissolved ions and reasonable hydraulic performance. Laboratory radionuclide testing at the University of Helsinki indicates excellent selectivity and very good kinetic behavior for both the CsFloc and CoFloc precoat materials. Based on these positive experiences, prototype composite filters have been manufactured in anticipation of plant trials. At this point, the alpha site testing of small cartridge composite filters in the radwaste system at TXU Comanche Peak SES is well underway. The results to date are quite promising. We anticipate presenting complete results of this work at a latter conference. In the meantime, Graver Technologies is seeking other opportunities for evaluation of composite filters in plant settings.

## ACKNOWLEDGEMENTS

Dr. Risto Harjula of the Laboratory of Radiochemistry, Department of Chemistry at the University of Helsinki has been a valued partner in this work. He and his colleagues performed all the radionuclide experiments in their laboratories. All of the data in the section entitled *Radionuclide Decontamination Trials Using Novel Precoat Materials* are directly attributable to Dr. Harjula and his group.

Mr. William Seeley of the Technology Department at Graver Technologies participated directly in the development of the filter portion of the composite filters. He offered insight and advice during the development and initial testing of these filters, in addition to his work on manufacturing prototypes.

Ms. Nichole Pennisi of the Technology Department at Graver Technologies performed all the preliminary evaluations of the three selective ion exchangers used as media components in the composite filters. As always, her work on this project was characterized by dedication and accuracy.

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## FOOTNOTES

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<sup>α</sup> Selion Oy is now called Fortum Engineering Services Oy.

<sup>β</sup> No CsFloc was included in this trial since none was available when the trial commenced.

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