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**MICROFILTRATION OF
RADIOACTIVE CONTAMINANTS**

MICROFILTRATION DES CONTAMINANTS RADIOACTIFS

L.P. BUCKLEY, J.A. SLADE, S. VIJAYAN and C.F. WONG

Chalk River Laboratories

Laboratoires de Chalk River

Chalk River, Ontario K0J 1J0

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RÉSUMÉ

Le traitement des liquides radioactifs par microfiltration tangentielle est en usage aux Laboratoires de Chalk River depuis environ quatre ans. Le procédé de séparation retire les particules en suspension des solutions de déchets radioactifs. On peut ensuite traiter le liquide propre au moyen de membranes utilisées dans la technique classique de l'osmose inverse pour obtenir des facteurs de réduction de volume approchant de 100. La microfiltration retire les particules dont la dimension est inférieure à 0,2 micron, en partie par agglomération des particules. On présente l'expérience d'exploitation avec un appareil à débit de 15 gallons américains par minute. En combinant la technique de microfiltration et le traitement chimique, on augmente le retrait des espèces solubles. On examinera l'expérience de Recherche et Développement avec le retrait de contaminants solubles trouvés dans les eaux souterraines et eaux résiduelles. Cette technique a des avantages sur d'autres techniques utilisant des membranes, à savoir: des coûts d'énergie plus bas, un degré d'encrassement inférieur et la récupération d'une plus grande quantité de solution traitée. On examinera les applications futures de la technique.

Systemes de gestion des déchets
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ABSTRACT

Cross-flow microfiltration processing of radioactive liquids has been in use at Chalk River Laboratories for about four years. The separation process removes suspended particles from radioactive waste solutions. The clean liquid can then be treated with conventional reverse osmosis membranes to achieve volume reduction factors approaching 100. Microfiltration removes particles below the rating of 0.2 microns, in part from particle agglomeration. Operating experience relating to a 15 USGPM unit is presented. Coupling microfiltration technology with chemical treatment enhances the removal of soluble species. Research and development experience with the removal of soluble contaminants found in ground water and waste water will be discussed. The technology has advantages over other membrane technologies, namely lower energy costs, a lesser degree of fouling, and a higher recovery of processed solution. Future applications of the technology will be addressed.

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1. INTRODUCTION

Radioactive liquid waste processing is integral to every facility involved in electrical power generation, radioisotope production, research and development, decontamination, remediation or other aspects of nuclear energy. Part of the focus of research and development effort in waste management at AECL is to evaluate, through demonstration, technologies applicable to the treatment of radioactive wastes. A facility was built at Chalk River Laboratories (CRL) to handle liquid and solid radioactive wastes generated at the site [1]. A treatment plant based on membrane separation technology was installed to process volumes of low levels of radioactive liquid.

The technology was originally based on volume reduction using reverse osmosis membranes, with pretreatment provided by ultrafiltration for colloidal and suspended solids removal. The ultrafiltration membranes were replaced four years ago with a microfiltration system. The system's success in handling a wide range of suspended solids prompted other investigations. The research and development programs that followed were an extension of previous work on ground water remediation and have been expanded to include the treatment of soil wash solutions. The programs have extended the capability of microfiltration to the treatment of soluble radionuclides, metals and organics. This paper describes the technology, discusses the current operation of the treatment facility at Chalk River Laboratories, and reviews technology development to remediate contaminated ground water. The success of the technology is in part due to advances achieved by the microfiltration manufacturer in providing a robust and reliable system. Plans for future development are also discussed, including integration with soil remediation projects and removal of metals from acid mine wastes.

2. MEMBRANE TECHNOLOGY BACKGROUND

Microfiltration has been used primarily to polish beer and wine, and for applications where sterile filtration is required, as when producing extended-shelf-life milk [2]. The technology utilized depth-type cartridges, where flow was directed through the filter material, which trapped the particles. The conventional flow path used was perpendicular to the filter material and all the solution processed passed through the filter material, creating a dead-end flow pattern. The dead-end filtration process required replacement of the filter material as it plugged, causing the pressure drops to become excessive.

In the early 1980's, manufacturers began to incorporate technology developed for reverse osmosis and ultrafiltration membranes to permit reuse of the filter [2,3,4]. First, membranes were manufactured to permit the capture of particles of a nominal diameter size, typically to 0.2 μm , but lower nominal particle size ratings have been achieved. The range of pore sizes is from 0.05 to 20 μm , permitting microfiltration membranes to remove microbes, bacteria, paint pigments and macromolecules with molecular weights greater than 300 000. Second, process schemes similar to those used for reverse osmosis and ultrafiltration were utilized, incorporating cross-flow, which sweeps the fluid parallel to the membrane surface. The advantage of cross-flow is the turbulent action of the solution, which helps to scrub the membrane surface, preventing it from plugging rapidly.

Microfiltration membranes are made from sintered metals, sintered ceramics and polymers. Cross-flow microfiltration membranes improved when they began to be constructed in a tubular or capillary form with high strength. This type of construction allows pressurizing from inside to outside or from outside to inside, enabling backflushing to take place. Backflushing is critical for continuous operation, so that high throughputs of solution can be maintained [5]. The fluid flux, flow per unit surface area will decline as the surface begins to collect particles and becomes fouled. The fouling can be minimized by regular sequences of backflushing (Figure 1), but eventually the process must be stopped and the membrane chemically cleaned to return the flux to higher values.

The cross-flow microfiltration system replaced the ultrafiltration units at CRL for several reasons: the quality of the ultrafiltration membranes led to higher-than-anticipated leakage of suspended solids, the membranes were not robust enough to withstand continuous backflushing demands, and the equipment was complex and difficult to maintain. The choice of the particular cross-flow microfiltration system over other processes available was based on the following reasons:

1. Minimum secondary waste arises from backflushing. The purchased unit has a unique, patented gas backflushing arrangement, which reduces the amount of water needed to clean the membranes. The filtrate is used as the source of backflush water and high recoveries of the feed solution can be realized.
2. Large throughput capacity. The surface area to volume ratio for the membranes was roughly 100 times better than the ultrafiltration membranes in use at the time. The microfiltration membranes are hollow fibre construction, versus the large tubular ultrafiltration membranes.
3. Robust membranes. The switch from cellulose acetate ultrafiltration membrane materials to polypropylene gives a wider latitude in operating conditions. The pH values of the solutions can range from 2 to 12 without detrimental effects. The membranes when fouled can be subjected to harsher cleaning solutions without chemically deteriorating.
4. Demonstrated industrial performance [6]. The operating history of the MEMCOR microfiltration membranes in wine-making confirmed the rugged construction of the membrane modules and, matched with the automated gas-liquid backwash system, showed that the system was capable of long periods of continuous, uninterrupted operation.

3. WASTE PROCESSING OPERATING EXPERIENCE

The cross-flow microfiltration technology adopted by AECL was developed by MEMCOR, and was originally purchased to provide high-quality feed water for the reverse osmosis system [7]. In 1988, a system was installed to process 40 000 L/week of radioactive liquid waste. The system has been handling nearly double that amount over the past few months. The liquid treatment system is shown schematically in Figure 2.

The quality of the filtrate water has been excellent; the average turbidity has been less than 1 NTU. As a bonus, in removing suspended solids, radioactivity has also been removed to varying degrees. At low pH values of 5 to 6, removal of the predominant radionuclides Co-60, Cs-137, and Ce-144 is observed (Table 1). These radionuclides are associated with colloids or are sorbed on the solid particles filtered out of the suspension. Since concern is for the delivery of a feed stream that minimizes fouling of the reverse osmosis system, pH adjustment of the incoming feed has been made to reduce the iron and silicon content. Iron and silica are well-known foulants of reverse osmosis systems. The adjustment of the solution pH values to the 10-10.5 range improved the quality of the filtrate and has permitted extended operation of the reverse osmosis system.

The reduction of iron has been observed at elevated pH values, along with additional reduction of Co-60 and Ce-144 (Table 2). The removal of Cs-137 did not increase, an expected result, since it is a highly soluble species and remained unaffected by the pH adjustment of the solution. Cobalt-60 removal was improved with the likely formation of cobalt hydroxide.

The microfiltration system has operated quite reliably over the nearly four years of liquid processing. Minor changes to optimize the backflush cycle have improved the recovery of feed and minimized the fouling of the membranes. The feed composition can vary quite dramatically, and additional operational skills have been acquired to minimize this impact on the operation and filtrate quality. The membranes have become quite fouled at times, with permeate fluxes (feed flow/unit membrane area) dropping by as much as 90% of the normal throughput.

In these circumstances, the membranes have had to be chemically cleaned to restore the permeate flux. Even with the use of aggressive cleaning agents, the original membranes are still in service. Two modules have been replaced in the four-year period. In each case, it was discovered, after runs in which the turbidity rose above a value of unity, that a couple of the hollow fibre membranes within the modules had broken from the repeated stress of backflushing. An easy mechanical test developed by the manufacturer pinpointed the affected modules and they were replaced within an operating shift.

A simple correlation exists between the activity in the feed to the microfiltration unit and the radiation field on the microfiltration modules. As shown in Figure 3, the relationship is quite linear, with contact radiation fields rising proportionally with increases in the beta-gamma activity of the feed solution. With this information, the operations personnel can determine how to combine the feed streams to monitor and maintain the radiation fields at a level that keeps the radiation dose under 1.0 Rem/a.

The equipment has proven to be robust, with low maintenance requirements, a high availability factor arising in part from the mechanical stability of the membranes, and excellent backflushing technology. Noticeable separation of radionuclides has been achieved and the operating performance of the reverse osmosis membranes downstream of the microfiltration system has improved with the improving performance of the microfiltration facility.

4. RESEARCH & DEVELOPMENT EXPERIENCE

The use of microfiltration to pretreat liquid to be processed by reverse osmosis demonstrated that radioisotopes attached to particles are effectively removed. Previous efforts to remove soluble species by adding polymers enabled the soluble radionuclides to be effectively extracted with ultrafiltration [8]. The attraction of the soluble radionuclides to the charged water-soluble polymers permitted the formation of a macromolecule that could be removed with a properly sized ultrafiltration membrane.

This previous knowledge of how to manipulate the solution chemistry, coupled with observations of the effectiveness of microfiltration, prompted a research and development program to establish how effective and appropriate separation of soluble species by microfiltration could be. One of the principal goals was to create size-enlarged particles that could be removed from solution using microfiltration technology. The shift away from ultrafiltration membranes was determined by the simpler, more robust technology offered by the MEMCOR system. The improved backwash system was an operating parameter key to the ultimate performance of the chemical treatment-filtration technology being proposed.

The second major reason for taking a chemical treatment approach was to remove soluble contaminants selectively from waste or ground water solutions. Reverse osmosis is a non-selective unit operation and, like distillation, removes all species whether they are hazardous or not. To avoid removing species that have no impact on the discharge quality of the effluent, which would increase the quantity of secondary wastes, selective removal is desirable. Chemical treatment is necessary to convert soluble radionuclides, trace organics and heavy metals to insoluble, filterable species. AECL adopted a variety of techniques to create size-enlarged species. These include, but are not limited to, additions of chemicals to cause precipitation, by additions of chemical additives that remove hazardous species by capture through co-precipitation, and by additions of high-surface area materials to permit adsorption, ion-exchange or absorption of the hazardous species.

Alteration of the chemical nature of the solution, allowing sufficient time for the radionuclides or other hazardous species to be sequestered selectively and for precipitates to grow or agglomerate, will permit the effective removal of contaminants from solution. For example, the addition of powdered zeolite, a naturally occurring mineral with known affinity for Cs-137, permits effective removal from solution by passing the mixture through a microfiltration membrane. This approach has been more effective than using a fixed-bed column of zeolite. The powdered zeolite has a higher surface to mass ratio, and so for the same mass of zeolite, more Cs-137 can be removed from solution, or alternatively, for the same volume of treated waste, less powdered zeolite is used, providing a smaller secondary waste volume for disposal. With a fixed-bed column, the zeolite media is generally replaced when breakthrough takes place. When high-quality water must be produced, the exiting concentration could result in poor utilization of the fixed-bed column material.

A test program involving both simulated waste solutions and actual field tests on ground water was undertaken, to generate high-quality effluent [9]. The work, performed for the United States Department of Energy, involved developing and demonstrating a process to remove different types of contaminants from solution. Pilot-scale test results, presented in Table 4, show that sequential treatment will remove contaminants from waste solutions and permit discharge of metals and radionuclides at levels below drinking water standards (Figure 4). A simplified version of the developed process has been successfully implemented at the Chalk River Laboratories site to remove Sr-90 from ground water.

The process has been patented [10]. The key chemical treatment steps include:

- pH adjustment by lime addition, combined with zeolite powder addition to precipitate, ion-exchange, adsorb and scavenge most of the heavy metals, along with iron and some radionuclides and organics;
- sequential addition of a natural zeolite ion exchange/adsorbent powder, to remove radionuclides, residual heavy metals and some organic contaminants; and,
- sequential addition of powdered activated carbon with or without zeolite powder as a polishing step, to remove organics and residual radionuclides.

The developed process has several advantages over conventional treatment techniques. There is direct contact of the contaminants while in solution with metal precipitates formed, and with powdered adsorbents and ion-exchange materials added to the solution. The added materials provide high contaminant removal through fast reaction kinetics. The materials added are low-cost by-products.

Continuous processing can be achieved with cross-flow microfiltration coupled to an air-backflush system. Steady-state operation is achieved quickly, and the modular construction allows for portability and a wide range of processing rates. Finally, the process is generic, to permit treatment of a wide variety of waste solutions. Included in future test programs is an evaluation of the technology for treating acid mine drainage wastes and further enhancements of ground water cleanup. The technology is suitable for inclusion in treatment trains for soil remediation; its potential for improving the efficiency of soil washing has yet to be explored.

5. CONCLUSIONS

The operating experience gained with cross-flow microfiltration for the removal of radioactive contaminants has demonstrated that the technology is versatile, and that the operation is simple and cost-effective, having low maintenance and operating expenses. Applied to the removal of contaminants in process streams, ground water, and soil-wash leachates, the combination of chemical treatment to create enlarged particles with microfiltration provides an effective process. Demonstrations of the technology show that it is reliable and capable of producing high-quality effluent, that scaleup is not difficult to achieve, and that the process is cost-competitive.

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Table 1
Waste Treatment Centre At CRL
Typical Contaminant Removal By Microfiltration Process

Species	Feed Concentration	Filtrate Concentration	Removal Efficiency (%)
Solution pH	<u>6.40</u>	6.30	
Co-60 (Bq/mL)	38.08	26.46	30.5
Cs-137 (Bq/mL)	131.10	118.40	9.7
Ce-144 (Bq/mL)	136.00	7.57	94.4
Gross beta/gamma	11610.00	4907.40	57.7
Iron(mg/L)	2.00	0.13	93.5
Turbidity (NTU)	21.00	0.37	98.2

Table 2
Waste Treatment Centre At CRL
Typical Contaminant Removal By Microfiltration Process

Species	Feed Concentration	Filtrate Concentration	Removal Efficiency (%)
Solution pH	<u>10.3</u>	10.30	
Co-60 (Bq/mL)	80.0	12.00	85.0
Cs-137 (Bq/mL)	325.0	308.50	5.1
Ce-144 (Bq/mL)	314.0	9.70	96.9
Gross beta/gamma	25000.0	728.50	97.1
Iron(mg/L)	8.4	0.10	98.9
Turbidity (NTU)	37.0	0.51	98.6

Table 3: Pilot-Scale Test Results for Contaminant Removal Using a Sequential Three Step Process (Figure 4) Involving Chemical Treatment-Microfiltration (Test No. SLZ4)

Description of Stream/ Parameter	Concentration of Metals and Organics in mg/L Concentration of Radionuclides in Bq/L									
	[Cd]	[Pb]	[U]	[Fe]	[Ca]	[Na]	[Sr-85]	[Cs-137]	[Benzene]	[TCE]
Feed	1.78	6.13	1.8	50.6	154	0.065	6180	3190	7.4	4.9
FWQI	178	122.6	30	168.67	0.77		41.2	862.16	1480	980
Process Step 1:										
Filtrate	0.0018	0.021	0.0039	0.019	134	9.55	4100	76.1	6.1	4
Process Step 2:										
Filtrate	0.0018	0.021	0.0039	0.015	2.05	230	21.5	8.06	3.8	2.1
Process Step 3:										
Filtrate	0.0018	0.021	0.039	0.0086	2.16	220	3.5	3.48	0.0624	0.0837
Process Step 1 + 2:										
% Removal	99.9	99.66	97.83	99.97	98.67	N.A.	99.65	99.75	48.65	57.14
(2s)	2.83	4.03	5.81	2.98	2.77		7.06	7.06	5.11	7.29
PWQI	0.18	0.42	0.65	0.05	0.01	N.A.	0.094	2.73	1220	1180
(2s)	0.014	0.014	0.071	0.005	0.0001		0.007	0.109	33.66	24.2
Overall: Process Step 1 + 2 + 3:										
% Removal	99.9	99.66	97.83	99.98	98.6	N.A.	99.94	99.89	99.16	98.35
(2s)	2.89	4.03	5.81	2.98	2.76		7.07	7.07	5.8	8.35
PWQI	0.18	0.42	0.65	0.029	0.01	N.A.	0.023	0.94	12.48	16.74
(2s)	0.014	0.014	0.071	0.0032	0.0001		0.0011	0.047	0.869	0.858

Note: The water quality indices FWQI and PWQI are defined as a ratio of contaminant concentration in waste feed (F) or in treated filtrate (F) to the maximum allowable concentration of the contaminant in drinking water under U.S. EPA regulations;
2s: 2 sigma statistics.

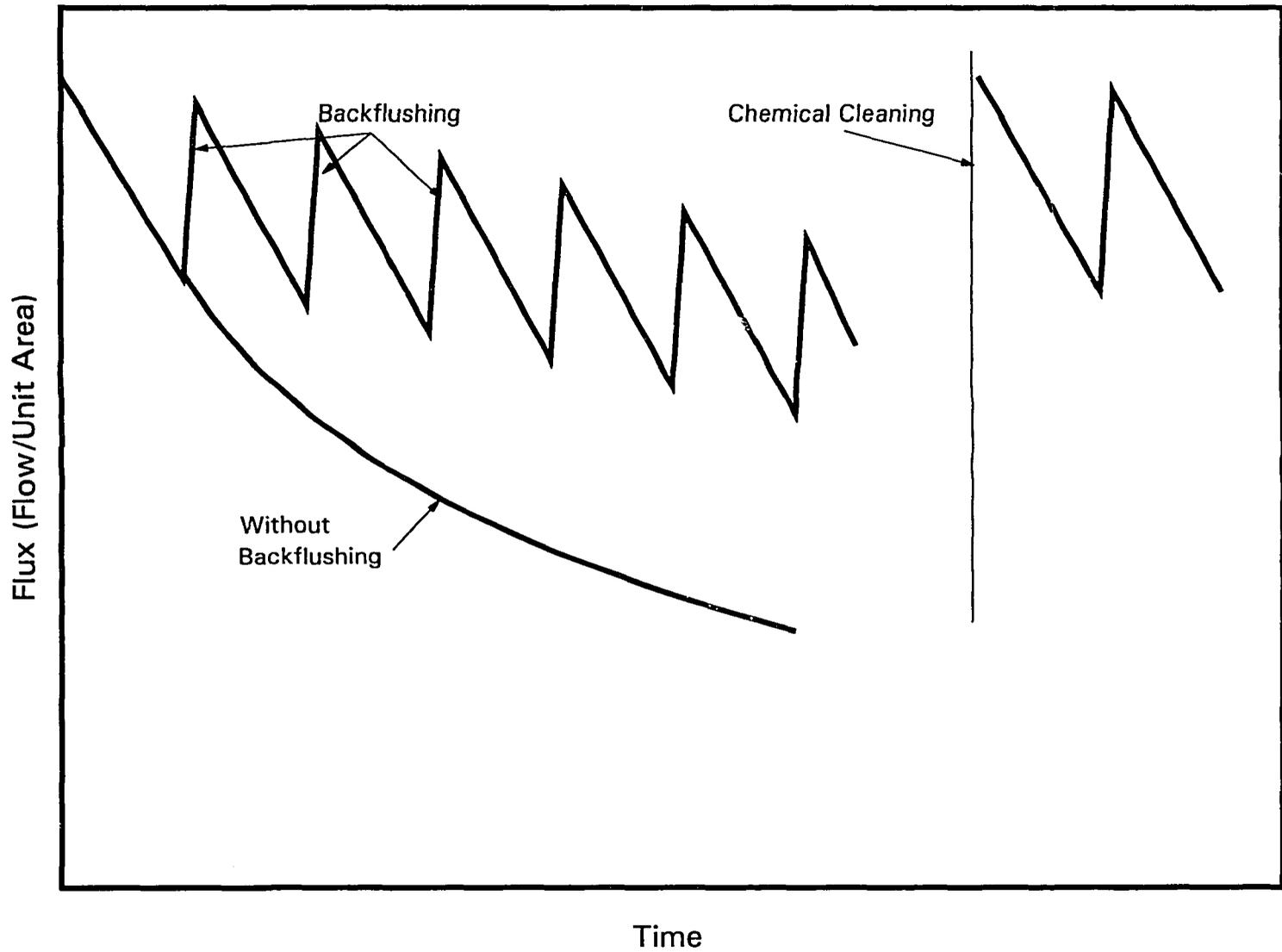


Figure 1: Cross-Flow Microfiltration Flux Performance

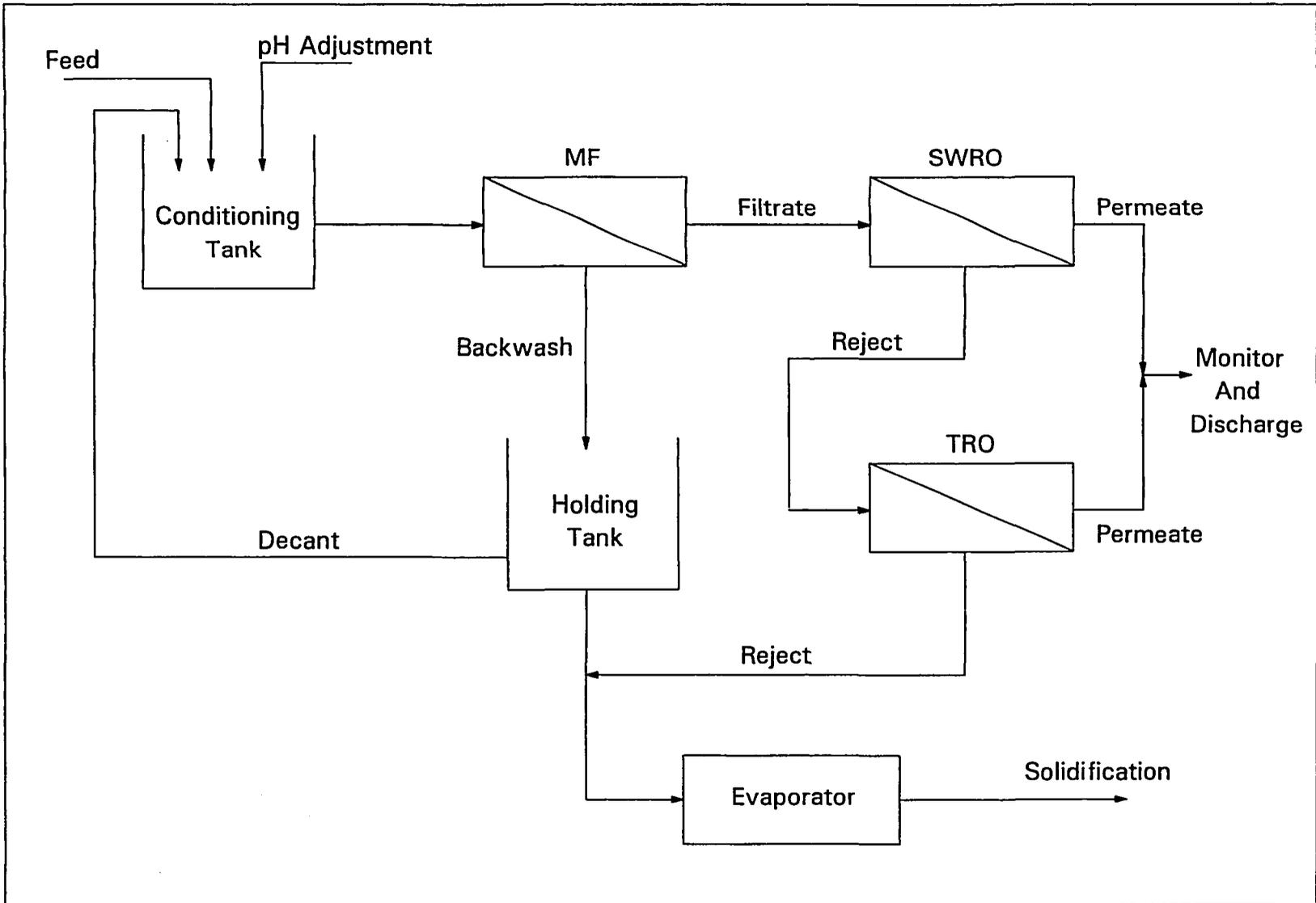


Figure 2: Waste Treatment Centre Process Diagram

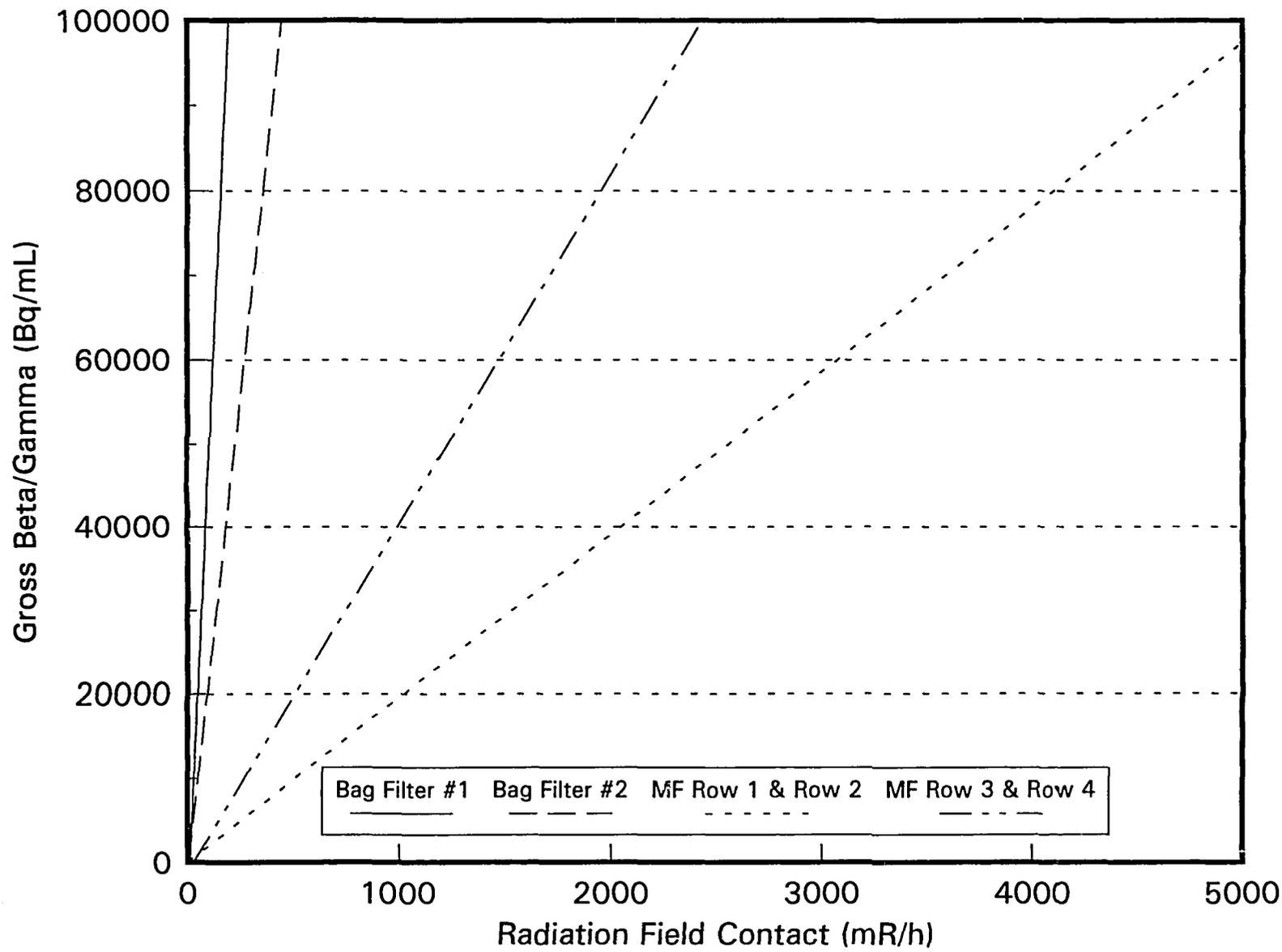


Figure 3: Contact Radiation Field On Microfiltration Bank A

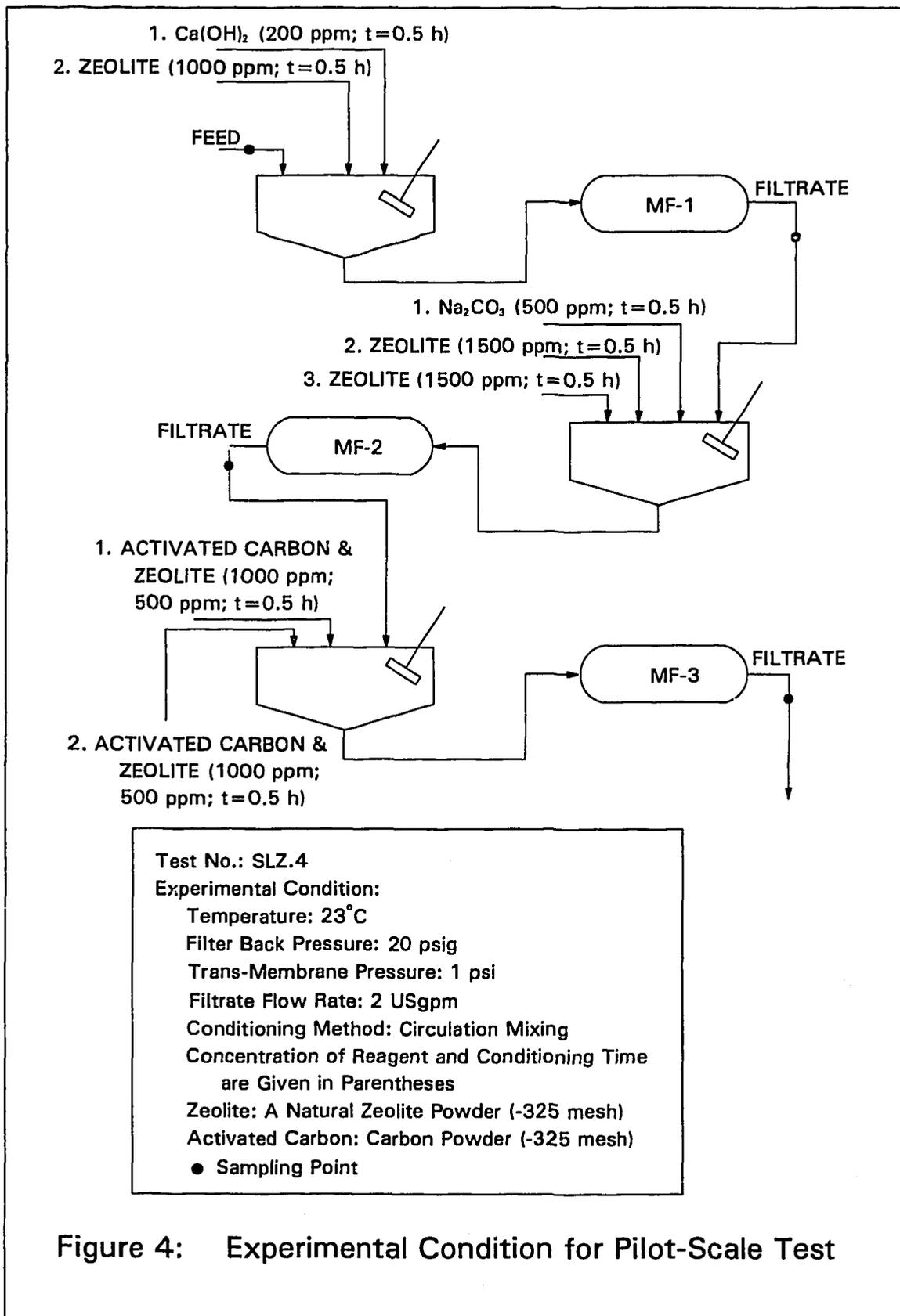


Figure 4: Experimental Condition for Pilot-Scale Test

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