

ATOMIC ENERGY
OF CANADA LIMITED



ÉNERGIE ATOMIQUE
DU CANADA LIMITÉE

REMOVAL OF SOLUBLE TOXIC METALS FROM WATER

ÉLIMINATION DES MÉTAUX TOXIQUES SOLUBLES DES EAUX

L.P. BUCKLEY, S. VIJAYAN, G.J. McCONEGHY, S.R. MAVES
and J.F. MARTIN

Presented at 16th Annual EPA Research Symposium, Cincinnati, Ohio, 1990 April 3-5

ATOMIC ENERGY OF CANADA LIMITED

**REMOVAL OF SOLUBLE TOXIC METALS
FROM WATER**

by

**L.P. Buckley, S. Vijayan, G.J. McConeghy and S.R. Maves
Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories**

and

**J.F. Martin, Risk Reduction Engineering Laboratory
United States Environmental Protection Agency**

**Presented at 16th Annual EPA Research Symposium, Cincinnati, Ohio,
1990 April 3-5.**

**Waste Management Systems
Atomic Energy of Canada Limited
Chalk River Nuclear Laboratories
Chalk River, Ontario, Canada KOJ 1J0**

1990 May

AECL-10174

ÉNERGIE ATOMIQUE DU CANADA

ÉLIMINATION DES MÉTAUX TOXIQUES SOLUBLES DES EAUX

par : L.P. Buckley, S. Vijayan, G.J. McConeghy et S.R. Maves
Énergie atomique du Canada limitée
Laboratoires nucléaires de Chalk River
Chalk River (Ontario) Canada K0J 1J0

et : J.F. Martin, Risk Reduction Engineering Laboratory
United States Environmental Protective Agency
26 W. Martin Luther King Drive, Cincinnati, Ohio 45268

RÉSUMÉ

On a réussi à éliminer certains métaux toxiques solubles de solutions aqueuses, à l'aide d'un procédé mixte de traitement chimique et d'ultrafiltration. Le procédé, d'abord étudié à l'échelle du laboratoire, est actuellement soumis à des épreuves à l'échelle de l'usine-pilote. On a atteint des rendements d'élimination de 95 à 99 %.

Le but du programme d'essai en laboratoire était d'étudier les limites et d'établir la plage optimale des paramètres utilisés pour l'application du procédé. Quant aux épreuves effectuées à l'usine-pilote, elles permettent d'obtenir des données sur les rendements du procédé à plus long terme, sur les taux d'efficacité du procédé de traitement et sur les possibilités de contamination par les membranes. Lorsque l'on utilise les eaux souterraines des sites de Superfund, présentant des concentrations moyennes de métaux toxiques typiques, comme solutions d'alimentation, le procédé réduit les niveaux de concentration par un facteur 1(0) au moins.

On a effectué certains essais sur des solutions concentrées afin de déterminer le niveau d'efficacité des matrices à base de silice. Les déchets solidifiés ont été soumis à des essais de toxicité EP et se sont révélés conformes aux critères établis. La phase finale du programme, consistant à faire une démonstration sur un site où se trouvent des résidus d'uranium, sera exposée dans ses grandes lignes.

La présente communication a été révisée selon les politiques d'examen par des collègues et l'administration de l'U.S. Environmental Protection Agency, et a été approuvée pour présentation et publication.

Systemes de gestion des déchets
Énergie atomique du Canada limitée
Laboratoires nucléaires de Chalk River
Chalk River (Ontario) Canada K0J 1J0

Mai 1990

A ECL-10174

ATOMIC ENERGY OF CANADA LIMITED

REMOVAL OF SOLUBLE TOXIC METALS FROM WATER

by: L.P. Buckley, S. Vijayan, G.J. McConeghy and S.R. Maves
Atomic Energy of Canada Limited, Chalk River Nuclear
Laboratories, Chalk River, Ontario, Canada K0J 1J0

and: J.F. Martin, Risk Reduction Engineering Laboratory,
United States Environmental Protective Agency,
26 W. Martin Luther King Drive, Cincinnati, Ohio 45268

ABSTRACT

The removal of selected, soluble toxic metals from aqueous solutions has been accomplished using a combination of chemical treatment and ultrafiltration. The process has been evaluated at the bench-scale and is undergoing pilot-scale testing. Removal efficiencies in excess of 95-99% have been realized.

The test program at the bench-scale investigated the limitations and established the optimum range of operating parameters for the process, while the tests conducted with the pilot-scale process equipment are providing information on longer-term process efficiencies, effective processing rates, and fouling potential of the membranes. With the typically found average concentrations of the toxic metals in groundwaters at Superfund sites used as the feed solution, the process has decreased levels up to 100-fold or more.

Experiments were also conducted with concentrated solutions to determine their release from silica-based matrices. The solidified wastes were subjected to EP Toxicity test procedures and met the criteria successfully. The final phase of the program involving a field demonstration at a uranium tailings site will be outlined.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administration review policies and approved for presentation and publication.

**Waste Management Systems
Atomic Energy of Canada Limited
Chalk River Nuclear Laboratories
Chalk River, Ontario, Canada K0J 1J0**

1990 May

AECL-10174

1. INTRODUCTION

Conventional treatment to remove contaminants from waste disposal sites or to prevent the spread of contaminant plumes is usually of the brute force mode, where large quantities of contaminated soils are excavated and treated by incineration, solidification, or other related technologies to remove, treat or detoxify the contaminants. In general, these large-scale technologies need to incorporate bulk material handling capabilities to accomplish the desired waste management.

An alternative to such material handling technologies is to remove the metal contaminants from the groundwater, through treatment to extract contaminants, and perhaps recycle the water to the contaminated zone to recover more contaminant adsorbed to the soils in contact with the groundwater. The technology proposed is a combination of chemical treatment and ultrafiltration to enhance the recovery of toxic metals from the water. The technology has been evaluated at the bench-scale level for the removal of radioactive cations from waste water streams (1,2). The technology appears suitable for the removal of toxic metal cations from contaminated groundwater surrounding industrial waste disposal sites and for the treatment of industrial effluents.

In the past year, chemical treatment in combination with ultrafiltration has been evaluated through funds allocated by the Emerging Technology Program of the United States Environmental Protection Agency (USEPA). The Emerging Technology Program, part of the Superfund Innovative Technology Evaluation (SITE), provides guidance and funding for new technologies which may become tools in the cleanup of environmental pollution. The two-year evaluation of the combined chemical treatment and ultrafiltration technique began by conducting experiments in laboratory-scale equipment, to verify the process capabilities for the removal of hazardous toxic metals which may be present in groundwater or industrial wastes.

Thus far, only four metals have been evaluated with the process. They are cadmium, lead, mercury, and arsenic; indicative of metals present in groundwater associated with hazardous waste disposal sites. The program to establish the viability of the process has progressed smoothly, results achieved from the program will be discussed, and proposed efforts to conclude the second year of the contract, which takes the technology through pilot-scale testing and field trials, are outlined.

2. TECHNOLOGY DESCRIPTION

The emerging technology reported here evolved through efforts by Atomic Energy of Canada Limited (AECL) to remove dilute concentrations of radioactive species from waste waters.

The process involves contacting the waste water with water-soluble macromolecular compounds added to the waste solution to form complexes with the soluble heavy metal ions. A high molecular weight polymer, generally a commercially available polyelectrolyte, is added to the waste solution to form the selective complexes. The polyelectrolyte quantities needed to achieve the separation of metal ions are generally in the parts-per-million range.

The solution is then processed through an ultrafiltration membrane system which retains the macromolecular complexes (retentate), while allowing uncomplexed ions such as Na^+ , K^+ , Ca^{++} , Cl^- , $\text{SO}_4^{=}$, NO_3^- , etc., to pass through the membrane with the filtered water (permeate). The filtered water can be recycled, or discharged depending upon the removal efficiency desired. A removal efficiency approaching 100% can be achieved for metal ions which have been complexed.

The technology as described can be applied to separate toxic heavy metal ions such as Cd, Cr, Hg, Ni, Cu, Zn, As and Pb from leachates generated in Superfund sites (3). Other inorganic and organic materials, if present as suspended and colloidal solids, can also be removed. The ultrafiltration membrane can be chosen with a sharp molecular weight cut-off, to further enhance separation. The toxic metals can be concentrated in a small residual volume which should be amenable to conventional solidification treatment.

3. BENCH-SCALE TESTS

3.1 Separation Studies

The first year of the test program was divided into five tasks: first, to evaluate the major variables using a factorial design having five variables, each at two levels, with fixed levels of metal contaminants; second, to study the extent of fouling and the cleaning techniques needed to recover the flux rate of the membranes; third, to evaluate the system response to changes in toxic metal concentrations; fourth, to perform a second evaluation of fouling and the cleaning techniques necessary to operate a continuous system; and fifth, to conduct a series of tests at three levels for each dominant variable, to optimize the technique for the removal of toxic metals.

The bench-scale tests were performed using Amicon ultrafiltration stirred cells. Cells with volume capacity of 50 mL or 200 mL, and equipped with rated membranes having molecular weight cut-off of 10 000, were used. The metal ions were complexed with polyelectrolytes, i.e., polyethylenimine, with a molecular weight of 50 000 and Gantrez AN 119, a polymethyl vinyl ether/maleic anhydride copolymer, of similar molecular weight. The operating conditions for the test series are summarized in Table 1.

TABLE 1. BENCH-SCALE EXPERIMENTAL CONDITIONS

Variable	Test Conditions	Test Conditions
Solution pH	alkaline	acidic
Membrane Type	polysulfone	cellulose acetate
Polyelectrolyte	polyethylenimine	Gantrez
Polyelectrolyte	10 times the	
Concentration, mg/kg	metal concentration	0
Toluene, mg/kg	1000	0

Cadmium removal efficiencies indicate that: the separation technique is more effective at elevated pH values; removal efficiency of about 99% can be obtained; and, it was difficult to distinguish the minor effects of other operating parameters such as membrane type, polyelectrolyte type and the presence of organics (toluene) on the removal efficiencies.

Removal efficiencies of 90% or higher were obtained for mercury. In contrast with cadmium, the removal of mercury is less affected by solution pH. Polyethylenimine appears to be a better complexing agent than Gantrez. Factors such as membrane type and toluene had no apparent effect.

Lead is a special case, because its starting concentration in the feed solution was two orders of magnitude higher than the other heavy metal ions examined in this study. Like cadmium, it is more effectively removed from solution at elevated pH values. However, the removal efficiencies are equally good when no polyelectrolyte was added to the feed solution, an indication that most lead is removed by precipitation as hydroxide.

Relatively poor separation efficiencies of <35% for arsenic were achieved with and without the addition of either polyelectrolyte. The reason is that a major fraction of arsenic is present in solution as an anionic species, i.e., AsO_4^{3-} , while most other metal ions are in the form of cations. The results obtained for arsenic indicate the present limitation of the proposed complexing polymers in the chemical treatment and ultrafiltration technique.

Polysulfone membranes experienced severe fouling, with permeation rates declining more than 70% when solutions containing polyethylenimine were treated. Gantrez caused less fouling to the polysulfone membranes, but the permeation reduction was also quite severe at high Gantrez concentrations.

Cellulose acetate membranes, in contrast, are essentially free from fouling caused by either electrolyte; only some slight fouling with permeation rate reductions of about 20-40% was experienced when either polyelectrolyte was used at a relatively high concentration in the lead test series. However, even with the limited fouling observed, the permeation rate of the cellulose acetate membranes is still five to ten times lower than achieved with the fouled polysulfone membranes.

Operating parameters such as pH and the presence/absence of toluene did not appear to have any impact on the fouling behaviours of the ultrafiltration membranes in these bench-scale tests.

Since the polysulfone membranes showed significant fouling in the first series of tests performed, only this type of membrane was used in a number of repeated tests to produce similarly fouled membranes, to evaluate the effectiveness of different chemical cleaning solutions. Four chemical cleaning solutions were compared: Tergazyme detergent; sodium hydroxide and hydrogen peroxide; methanol acidified with hydrochloric acid; and, deionized water as the control cleaning solution.

In each test, a membrane was subjected to a pure-water test to obtain the initial permeation rate. Ultrafiltration of the test solution containing metal polymer complexes followed, to obtain a water recovery of 90%. Then, the following steps were taken: rinsing with deionized water, cleaning with one of the chemical solutions, and, finally, re-rinsing with deionized water. At the end, a pure-water test established the post-test permeation rate.

The results indicate:

For a polysulfone membrane fouled by polyethylenimine, acidified methanol is the best cleaning solution to restore the permeation rate. Tergazyme detergent caused further severe fouling to the polysulfone membrane which had already been fouled by polyethylenimine. The detergent may contain an anionic surfactant which reacts with the cationic polyelectrolyte, to form an insoluble product which plugs the membrane pores. Sodium hydroxide-hydrogen peroxide did not remove the foulant better than deionized water.

For a polysulfone membrane fouled by Gantrez, cleaning with deionized water was able to restore most of the permeation rate. Overall, it is easier to remove this polyelectrolyte than polyethylenimine from the fouled polysulfone membrane. Acidified methanol was less effective, while the other two cleaning solutions are slightly more effective than deionized water.

The repeated tests performed for the membrane cleaning tests provided an opportunity to check the reproducibility of the performance of the chemical treatment ultrafiltration combination technique. The results indicated that relatively consistent results such as separation efficiencies, permeation rates and permeation reduction can be reproduced for tests carried out under the same operating conditions with different membranes.

The performance of this separation technique may be affected by the variability of the feed concentrations of the metal ions. Varying the dissolved metal concentration in a feed solution represents a realistic situation where the separation process is applied using a predetermined set of operating conditions. Metal separation efficiencies, membrane fouling behaviour and the effect of chemical cleaning were studied. Polysulfone membranes were chosen to allow the study of membrane fouling and cleaning. An alkaline solution pH value was selected to get high removal efficiencies for the heavy metals. No toluene was added to the feed solution, since the earlier tests did not indicate any adverse effects of separation when toluene was present or absent.

The test program produced optimum conditions for the dominant variables and provided additional verification of the process to remove soluble metal cations from solution. The addition of excessive amounts of polyelectrolyte did not enhance the separation observed from the first series of experiments. Variation of the pH values improved the separation, but again, at increasing alkalinity levels, the improvement in the separations observed were minimal. Finally, further evaluation of the polyelectrolyte selection did not produce large enough differences to dominate the selection for the pilot-scale tests.

3.2 Solidification and EP Toxicity Tests

Next, a solidification study was performed on some of the concentrated waste products generated from several of the above tasks, specifically to establish the success in producing a quality product which will be strong enough to survive the structural integrity procedure in the EP Toxicity procedure, and provide concentrations of the contaminants below the limits set out in Table 1 of 40 CFR 261.24 (4). Whether the concentrated waste had a harmful effect on the matrix stability or its ability to retain heavy metals had to be resolved.

There were three matrices chosen, all cementitious-based to immobilize the concentrated product which will arise from the volume reduction of the waste solutions treated by the ultrafiltration membranes. The three matrices were: ordinary Portland Cement, Type I (OPC); Aquaset, a proprietary product of Fluid Tech, Inc.; and a mixture of OPC and blast furnace slag. Products were prepared with ten- and twenty-fold increases in metal and polyelectrolyte concentrations, typically expected from recycle of the waste solutions through an ultrafiltration system. The samples were molded and then cured for periods of seven days. The samples were released from their molds, each in turn placed in a compaction tester to establish the structural integrity of the specimen, and then subjected to the EP Toxicity test procedures (4).

Results are available at this time for only the OPC specimens. All formulated specimens successfully passed the structural stability test, allowing the specimens to be leached intact. The test matrix included both electrolytes and metal concentrations at ten and twenty times the average feed concentration. The measurement of metal content of the leachates indicated the levels were less than the detection limits available for the analytical instruments used, and well below the maximum concentration of contaminants characteristic of EP toxicity listed 40 CFR 261.24 (4).

4. PILOT-SCALE TESTS

A schematic of the pilot-scale test facility is presented in Figure 1. The ultrafiltration membranes used were purchased from the Romicon and Amicon corporations. The modules (or cartridges) are constructed with hollow fibre membranes, and made with polysulphone. The Amicon module has twice the surface area of the Romicon unit.

A hollow fibre configuration for the ultrafiltration membrane system was selected because of its many attractive features (5). These include: high surface area-to-volume ratio; low holdup volume; low energy consumption; and relatively easy cleaning by "backflushing". Minor disadvantages include higher membrane replacement costs and susceptibility to plugging.

The choice of polysulphone material for the membrane was based on the high flows capable with this material, compared to that of cellulose acetate, in spite of the increased fouling of the polysulphone membranes observed in the first test phase. Other reasons for the choice were the operating range established from the first series of tests, which indicated alkaline conditions were better, and to overcome the distinct possibility of poor lifetimes expected of cellulose acetate at elevated pH levels.

The pilot-scale test program was established to obtain engineering design data to permit the building of the field test unit, and to permit some initial cost evaluations to be undertaken. Tests were of three general types to evaluate the operation of single membrane modules: first, in a batch mode, by continuous recycle of both permeate and retentate streams to the feed tank, to establish the separation efficiency; second, in a concentration mode, enriching the feed by allowing the permeate to be discharged from the system while recycling the retentate to the feed tank; and third, in a feed and bleed mode, where fresh feed is introduced to the system while simultaneously removing concentrate and permeate, with the bleed-to-permeate ratio fixed by the specified recovery.

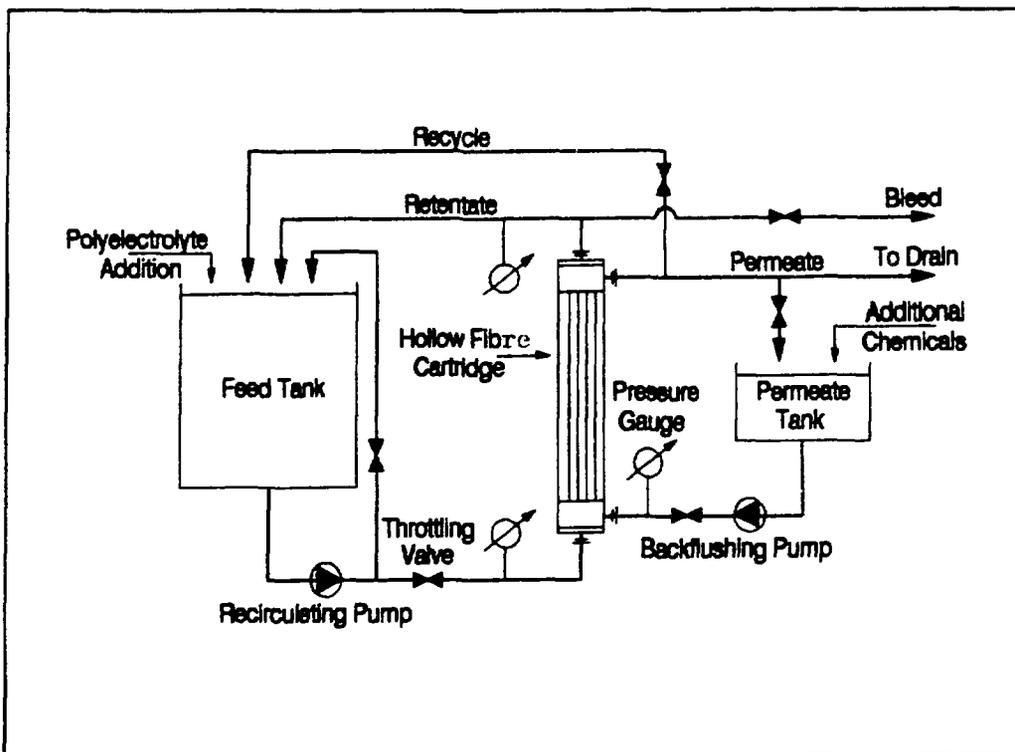


Figure 1. Schematic of pilot-scale unit

The operating conditions for the three types of pilot-scale tests are given in Table 2.

TABLE 2. PILOT-SCALE EXPERIMENTAL CONDITIONS

Variable	High Value	Low Value
Solution pH	alkaline	neutral
Membrane Surface Area (ft ²)	30	15
Operating Pressure (psig)	45	25
Feed Rate (US gal/day)	6500	4000
Polyelectrolyte Concentration (ppm)	10 times the metal concentration	0
Metal Concentration in feed (ppm)	10 times the low value	0.5, 0.3, 60

[cadmium, mercury and lead]

Most experiments covering batch and concentration modes of operation are complete. The majority of analytical results for the separation efficiencies of the heavy metals are pending. Preliminary analysis of some analytical results for batch-mode tests have revealed removal efficiencies in the range of 85-99% for lead, mercury and cadmium from a combined alkaline feed stream. The analysis of organic content of the permeate water indicated that most, if not all, of the polyelectrolyte is being removed from the feed stream by the membranes. The feed flow rate was 4000 US gal/day and permeate flux varied from 30 to 75 US gal/ft² day. Unlike the bench-scale test results, the initial pilot-scale data showed appreciable loss of metals. It appears the loss is due to adhesion, adsorption, and free settling of metal complexes and precipitates within the process equipment. Methods to account for and minimize losses, and to recover the metals, are being studied.

The hydraulic behaviour of the new membranes after a few days of usage produced a steep drop in the permeation rate of about 30%, mainly due to compaction of the membranes. After this initial irreversible decrease, the permeate rate decreased more slowly, eventually reaching a point where backflushing or chemical cleaning was necessary to recover the flux to reasonable levels. Once removal of the polyelectrolyte begins, additional permeate flux loss is evident (see Figure 2). The loss becomes more dramatic when alkaline feed solution containing lead is concentrated. A permeate flux loss of up to 75% from membrane compaction, physical ageing by extended operation, and by plugging of pores by particles, was not uncommon in the pilot-scale tests. These flow results confirm the initial bench-scale studies performed with flat membranes.

5. DEMONSTRATION TESTS

The demonstration tests are expected to take place at a site near the town of Elliot Lake, Ontario, about 400 km from the Chalk River Nuclear Laboratories site. A substantial quantity of uranium mine tailings was deposited within the property boundaries during operation of the Nordic Mine by Rio Algom Limited from 1957 to 1968. The waste, while mildly contaminated with residual quantities of uranium, radium and thorium, also contains other metal ions including iron, calcium, magnesium, aluminum, copper, cobalt, zinc, lead, nickel, chromium and cadmium. The tailings impoundment has been investigated to determine the migration of acidic groundwater seepage. While the contaminated groundwater does not constitute a hazard because of its remote location and limited migration of the heavy metals and radioactive ions (6), it provides an opportunity to field test the developing technology.

The project involves building a mobile facility capable of treating about 30 L/min of contaminated groundwater. After commissioning the mobile unit, it would be transported to and operated at the tailings impoundment. The technology will be assessed to determine its potential to decontaminate a plume of toxic metal ions released in the groundwater from the tailings impoundment.

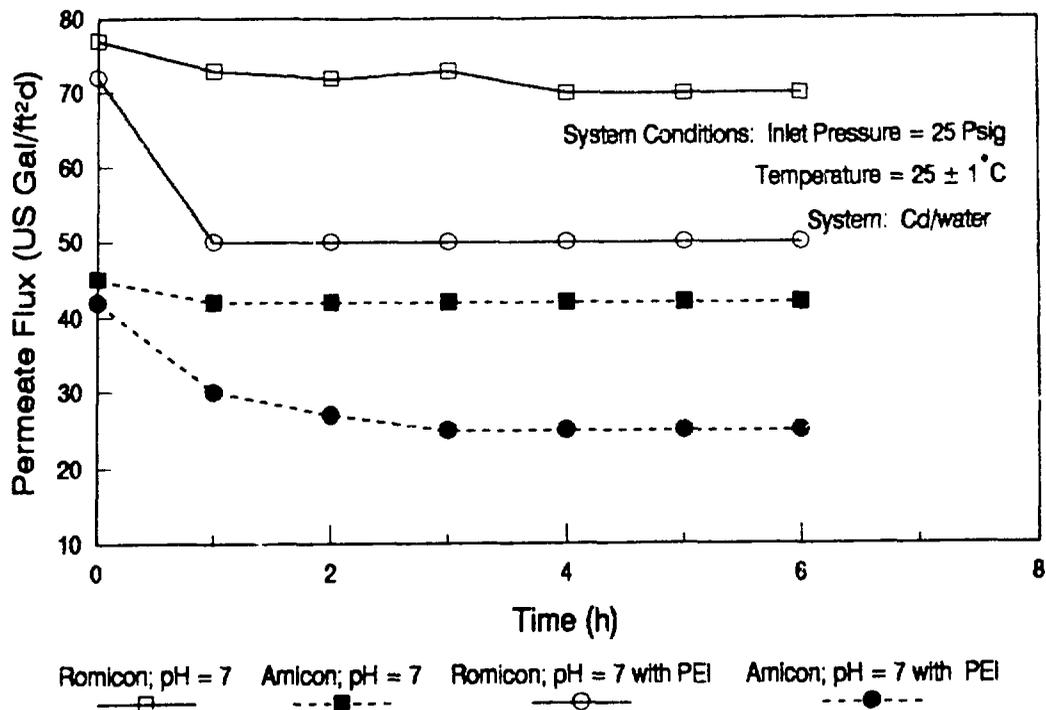


Figure 2. Permeation rates of hollow fibre modules

6. CONCLUSIONS

Based on the tests performed thus far, we can state:

- Among the four heavy metals examined, cadmium, lead and mercury are effectively removed (99%), while arsenic removal was less effective.
- Separation of heavy metal ions is better in an alkaline medium than in an acidic medium and membrane composition is not a major factor.
- The presence of toluene in feed water does not seem to affect the metal separation efficiency nor the membrane fouling rate, although its effect on membrane integrity during extended operation must not be ignored.
- Initial data from the pilot-scale studies have confirmed high separations are achievable and design data are available for the field test facility.

In summary, the proposed technology could be applied to remove selectively toxic metal ions from the Superfund site leachates. The residual volume produced in this technique is significantly smaller than volumes achieved in other conventional water treatment techniques, such as evaporation, ion exchange and reverse osmosis, where large quantities of non-toxic ions are also included in the concentrated products. Significant savings may be realized due to the reduction in the final volume of the stabilized product that needs to be disposed of. Even though it is not a stand-alone treatment process, this chemical/ultrafiltration combination method may contribute to a

cost-effective scheme which integrates a number of separation processes to provide treatment for complex waste streams. The proposed technology may be utilized to provide in-situ cleanup of contaminated soils, by extracting the contaminants from the groundwater, and by recycling the water to the contaminated zone to recover more contaminant adsorbed to the soils.

7. ACKNOWLEDGEMENT

The tests described and the resulting data in this paper were obtained from research conducted by Atomic Energy of Canada Limited and sponsored in part by the U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, under Federal Grant number CR-815321-01-0.

8. REFERENCES

1. Le, V.T., Buckley, L.P., and McConeghy, G.J. Selective removal of dissolved radioactivity from aqueous wastes by a chemical treatment/ultrafiltration technique. Presented at the International Conference on Separations Science and Technology, Hamilton, Ontario, October 1989; also Atomic Energy of Canada Limited Report AECL-9861, June 1989.
2. Buckley, L.P., Le, V.T., McConeghy, G.J., and Martin, J.F. Selective removal of dissolved toxic metals from groundwater by ultrafiltration in combination with chemical treatment. Presented at Haztech International '89 Conference, Cincinnati, Ohio, September 12-14, 1989; also Atomic Energy of Canada Limited Report AECL-10030, September 1989.
3. Josephson, J. Implementing Superfund. Environ. Sci. Technol., Vol. 20, No. 1, pp.23-28, 1986.
4. Code of Federal Regulations Protection of Environment Title 40, Part 261, Appendix II, "EP Toxicity Test Procedures", U.S. Government Printing Office, 1987.
5. Cheryan, M. In: Ultrafiltration Handbook. Technomic Publishers, Lancaster, 1986. pp 144-151.
6. Morin, K.A., Chery, J.A., Dave, N.K., Lim, T.P., and Vivyurka, A.J. Migration of acidic groundwater seepage from uranium-tailings impoundments, 1. Field study and conceptual hydrogeochemical model. Journal of Contaminant Hydrology, 2: pp 271-303, 1988.

ISSN 0067-0367

To identify individual documents in the series
we have assigned an AECL- number to each.

Please refer to the AECL- number when re-
questing additional copies of this document

from

Scientific Document Distribution Office
Atomic Energy of Canada Limited
Chalk River, Ontario, Canada
K0J 1J0

Price: A

ISSN 0067-0367

Pour identifier les rapports individuels faisant
partie de cette série nous avons assigné
un numéro AECL- à chacun.

Veuillez faire mention du numéro AECL- si
vous demandez d'autres exemplaires de ce
rapport

au

Service de Distribution des Documents Officiels
Énergie atomique du Canada limitée
Chalk River, Ontario, Canada
K0J 1J0

Prix: A