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Final Report

GSRI Project No. 323-673-11

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DEVELOPMENT AND EVALUATION OF ION EXCHANGE HOLLOW FIBERS

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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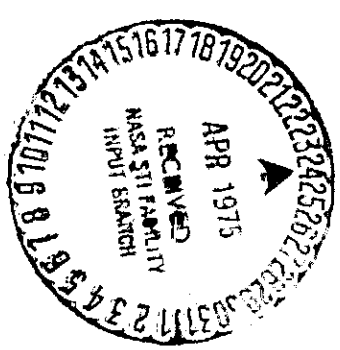

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PREFACE

This report is submitted in final fulfillment of NASA subcontract NAS 7-100,953874, Modification #1 to develop and evaluate ion exchange hollow fibers.

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ION EXCHANGE HOLLOW FIBERS

INTRODUCTION

In 1924, F. G. Donnan (1) summarized the thermodynamic equilibria governing systems in which one component is excluded from distributing throughout the system by a semipermeable barrier. From Donnan's studies, there developed a general description of the behavior of solutions separated by a barrier impermeable to at least one species. The terms Donnan dialysis, Donnan potential and Donnan equilibrium all describe the responses of systems wherein one component is excluded from a portion of the system.

According to the Donnan equilibrium statements, there will occur instances in which a solute is driven in the direction of its electrochemical potential difference, which may be opposite to its concentration gradient. While the study of the kinetics and thermodynamics of excluded systems has continued since the work of Donnan, the application of these principles to industrial process use has been rather minimal. Since 1967, Wallace (2), Davis (3), Smith (4) and Melsheimer (5) have considered the potential of Donnan dialysis for specific applications. These studies have indicated that the utility and economics of the process will depend primarily on the rate at which ions can be made to move across the semipermeable barriers, and the degree of exclusion that can be maintained for the "driving" species. In a recent assessment of the economics of water softening (6), Dressner specifically indicated that a reduction in membrane thickness is required to provide an economic advantage.

The present study was designed to develop an ion exchange barrier that meets these criteria. The Gulf South Research Institute (GSRI) effort was designed to provide a thin-walled hollow fiber that can be impregnated with an ion exchange resin. The sponsor's efforts were desinged to provide the means and/or method of [illegible]ation. This report contains the results of the GSRI study.

An ion exchange hollow fiber impregnated with a vinylpyridine base has been prepared by Gulf South Research Institute. The basic exchange resin used to impart the necessary permselectivity to the hollow fiber is a copolymer of vinylpyridine and dibromoethane prepared according to Rembaum et al. (7). A slight pressure is used to impregnate the exchange monomer mixture into the void structure of the fiber wall, and with maintenance of subambient temperatures, the rate of cross-linking is slow enough to allow the growing polymer to permeate the wall structure before significant increase in polymer molecular weight. When the fiber is returned to room temperature, the cross-linking automatically accelerates. The curing can be quickened even more by elevating the temperature or by use of γ irradiation.

These ion exchange fibers are produced from polyacrylonitrile hollow fibers with an appropriate wall structure that enables the impregnating vinylpyridine monomer mixture to form a truly semipermeable anion barrier after curing.

THE SPINNING OF HOLLOW FIBERS

Our hollow fibers are continuously spun from a polymer solution of suitable viscosity and gelling properties. When the fiber is quenched, a dimensionally semistable structure is produced. The polymer solution is extruded from an orifice into the open atmosphere and shortly thereafter the fiber is drawn through a quench bath. Various properties may be imparted to the hollow fiber by variations of the composition of the bath. The bore of the fiber is kept open by use of liquid or gaseous materials which further determine structure and thus transport properties of the fiber wall.

Although these variables complicate the spinning process, they more importantly lend tremendous versatility to the process by enabling the production of fibers with a wide range of pore structures and resulting transport properties. The choice of effective pore size in the wall of the hollow fiber is an important criterion because the vinylpyridine is much more likely to be leached from a large, coarse pore structure than from a fine, more selective one. If the void structure is too small, then

later ion flux rates will suffer, and impregnation of the exchange mixture will be less efficient and more difficult. If it is desired, the hollow fiber can be further modified by a heat treatment which alters the wall polymer structure. Such heat treatment also can adjust the size and shape of the pores of the fiber wall.

The physical dimensions of the fibers can be varied over a fairly large range. Internal diameters vary from 100 microns to greater than 800 microns and wall thicknesses range from 30 to greater than 200 microns depending on the polymer system and internal diameter.

We can produce a single continuous hollow fiber with transport properties and dimensions that can be varied by the spinning conditions. The fiber properties may be varied further by post production treatments, such as heat or chemical alteration, and impregnation with other non-leachable polymers.

THE POTTING OF HOLLOW FIBERS

Once produced, the hollow fibers need to be arranged into an ultimately useful form. One advantage of the hollow fiber configuration is that a large effective surface area can be obtained in a small volume. There are three ways in which the effective area can be increased: (1) the fiber length can be increased; (2) the fiber diameter can be increased; or (3) the number of fibers can be increased. When other factors, such as pressure drops across the length of the fiber bundle, are considered, the only important way to increase the total surface area is to increase the number of fibers and keep the length and diameter small.

Construction of a bundle of hollow fibers requires formation of a dam at the end of the fibers to allow simultaneous access to the bores of all the fibers but at the same time to prevent any leakage of the bore test fluid into the area outside the fibers. We have found that the difficulty of successfully building these dams greatly increases with the number of fibers to be incorporated into the bundle.

Several materials, ranging from silicone resins to various polyurethanes and epoxies, have been used in the preparation of these dams. We have

successfully prepared bundles of 150-200 fibers with both polyurethane and silicone dams. Restrictions on potting compounds, determined by the chemical solubilities of the damming materials in their proposed working environments, have been encountered. Further work is underway on the procedure of scaling up the potting process and on the development of other, possible more suitable, potting materials.

Fiber bundles can be prepared with virgin fiber as it is produced from the spinning line, or from fiber that has been pretreated to have more desirable properties. Alternatively, the completed bundle can be chemically or physically altered to achieve the best fiber.

HOLLOW FIBER BUNDLE TESTING

Hollow fiber bundles are first subjected to a series of screening tests to characterize the important properties of the fibers. If the basic properties are promising, then other tests may be run to broaden the characterization.

Initially, all bundles are tested for gross leaks of either the potting material or the fibers themselves. This test is accomplished by blowing all water from the fiber bores and then plugging one end of the bundle and maintaining 4-6 psi air pressure on the other end. When the whole bundle is submerged into a water bath, all leaks will immediately become obvious. When a bundle has passed the general leak test, its hydraulic permeability is measured. This measurement gives a general indication of the porosity of the fiber. Then, depending on the information desired, one or more of the characterization tests (Table 1) for the treated and untreated bundles may be performed.

TABLE I

HOLLOW FIBER CHARACTERIZATION TESTS

Untreated Bundles	Treated Bundles
1. Dimensions	1. Hydraulic permeability
2. Hydraulic permeability	2. NaCl leakage
3. Void volume	3. Donnan pumping experiments
4. THO diffusion	4. Void volume
	5. THO diffusion

1. Hydraulic Permeability Tests

The hydraulic permeability test is performed only after a fiber bundle has been checked for leaks. A bundle with a known number of fibers of known inner and outer diameter is flushed with distilled water. The bundle is then placed into a fixed configuration, and the bores of the fibers are filled with distilled water. One end of the bore is plugged, and a regulated pressure is applied to a water supply on the other end. The permeability is determined from the following relation:

$$L_p = \frac{1}{A\Delta P} \frac{\Delta V}{\Delta t}$$

where A = effective surface area (cm^2)

ΔP = pressure (atm)

ΔV = volume loss from the reservoir, or volume of water passed through and out of the fibers (cm^3)

Δt = time interval of the ΔV volume measurement

L_p = hydraulic permeability coefficient (cm/sec-atm)

2. Fiber Dimensions

Dimensions of the hollow fibers are determined by microscopic examination. The fibers are fixed into imbedding wax, and thin cross sections are cut with a microtome. The section is then viewed through a microscope and the dimensions are determined by the use of a superimposed scale in the eyepiece. At this time, gross macro structure in the hollow fiber wall can be noted.

3. THO Diffusion

The permeability of tritiated water (THO) through the fiber wall is determined with the fiber bundle mounted in the Donnan dialysis test apparatus shown in Figure 1.

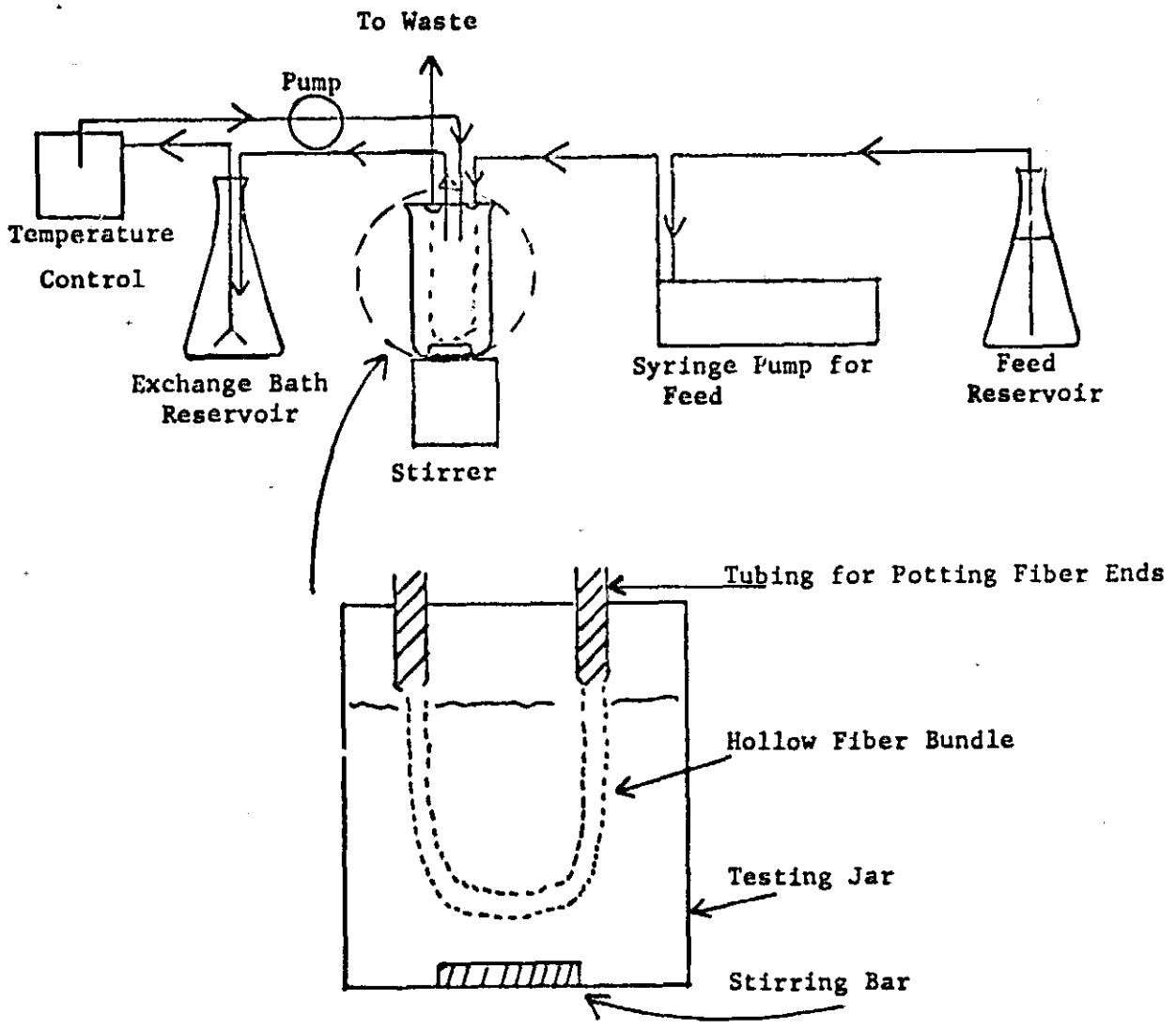

Figure 1. Donnan Dialysis Test Apparatus.

The permeability is calculated from data on the inlet and outlet concentration of THO feed passing through the fiber bundle.

$$P_{obs} = \frac{Q}{A} \ln \frac{C_{in}}{C_{out}}$$

where P_{obs} = observed permeability of the monitored exchanging species (cm/sec)

Q = flow rate of the bore feed (cm^3/sec)

C_{in} = concentration of monitored species into fiber bore

C_{out} = concentration of monitored species out of fiber bore.

4. Determination of Fiber Void Volume

The usual procedure for determining the water content of polymeric fibers is to remove all surface water by blotting and to determine the weight of the imbibed water with wet and dry measurements. Due to the uniqueness of the hollow fiber configuration, a special technique has been developed for removal of the surface water. The fibers (in an inverted U configuration) are placed in a centrifuge tube to a depth at which the fiber ends do not touch the liquid level when centrifuged. The tube is sealed to prevent the fiber from drying. After centrifuging, the fibers are removed from the tube and placed into a tared, sealed weighing jar and weighed while wet. The jars are then opened and the fibers dried at 80°C to a constant dry weight. They are then reweighed. The void fraction is then determined by the following relation:

$$\text{Void fraction} = \frac{\text{volume } H_2O}{\text{volume polymer} + \text{volume } H_2O}$$

$$= \frac{\text{Wt. } H_2O/\rho\ H_2O}{\text{Wt. polymer}/\rho\ \text{polymer} + \text{Wt. } H_2O/\rho\ H_2O}$$

EXPERIMENTAL RESULTS

The basic properties of polyacrylonitrile hollow fibers before and after treatment with vinylpyridine ion exchange resin are shown in Table 2. From this table it can be seen that the hydraulic permeability and related THO diffusion and void fraction decrease after treatment. The values of these three properties decrease when the exchange resin is polymerized in the fiber wall structure, because the resin occupies some of the void space of the basic fiber.

TABLE II

BASIC PROPERTIES OF POLYACRYLONITRILE HOLLOW FIBERS BEFORE AND AFTER TREATMENT WITH ION EXCHANGE RESIN

Polyacrylonitrile Fiber	L_p (cm/sec-atm x 10^5)	Dimensions (microns)	THO Diffusion†	Void Fraction*
Untreated	7.21	OD-490		
		ID-270		0.55
Treated	0.92	OD-440	2.98 x	<0.10‡
		ID-220	10^{-5}cm/sec	

† For an ion exchange type fiber before and after treatment.

* Based on a density of 1.16 g/cc for polyacrylonitrile.

‡ When the void fraction becomes very small the errors involved in the analysis increase greatly.

Figure 2 shows the molecular weight cutoff of a typical synthetic polymeric hollow fiber material. From this figure one can see that if any exchange resin is to be impregnated in the wall structure the pre-polymer molecule must be of a size suitable to allow a significant quantity of resin to penetrate in a reasonable time period. It should also be noted that the resin, once impregnated, has to be cross-linked or that its molecular weight has to be built up sufficiently to prevent leaching under operating conditions.

The potential of the Donnan process employing these ion exchange hollow fibers is shown in Figure 3. This experiment was designed with a continuous fresh feed of 10 ppm chromate solution. The product was fed to waste after the effluent concentration was monitored. A pump solution of 3% NaCl was employed to facilitate transport of the chromate ion. This solution was maintained at a fixed volume with no makeup during the experiment. The data presented show the first eight hours of the run. Additional data were obtained each day for one week. The same pattern of results was observed throughout the experiments. The concentration of the feed solution was reduced approximately 80% in a one-pass flow-through configuration. The concentration of chloride ion in the effluent was higher than predicted from the mass balance required to achieve pumping, indicating some leakage through the fiber wall. However, the transport of chloride into the chromate stream remained constant during the run and good pump rates were observed. The concentration of chromate in the pump solution was allowed to build up to approximately 1,000 ppm. Even at these levels of chromate in the pump solution, no appreciable reduction in the pumping efficiency was observed.

The leaching of exchange resin from the "cured" exchange bundle can be significant. Table 3 shows the loss of capacity of hollow fibers impregnated with an exchange resin and cured in two different manners. The capacity determinations were made after the fibers were washed in tap water for the allotted time period.

TABLE III

HOLLOW FIBER EXCHANGE CAPACITY

Type	Initial Capacity (meg/cc)	Capacity after 21 Days
1	1.79	0.52
2	0.86	0.52

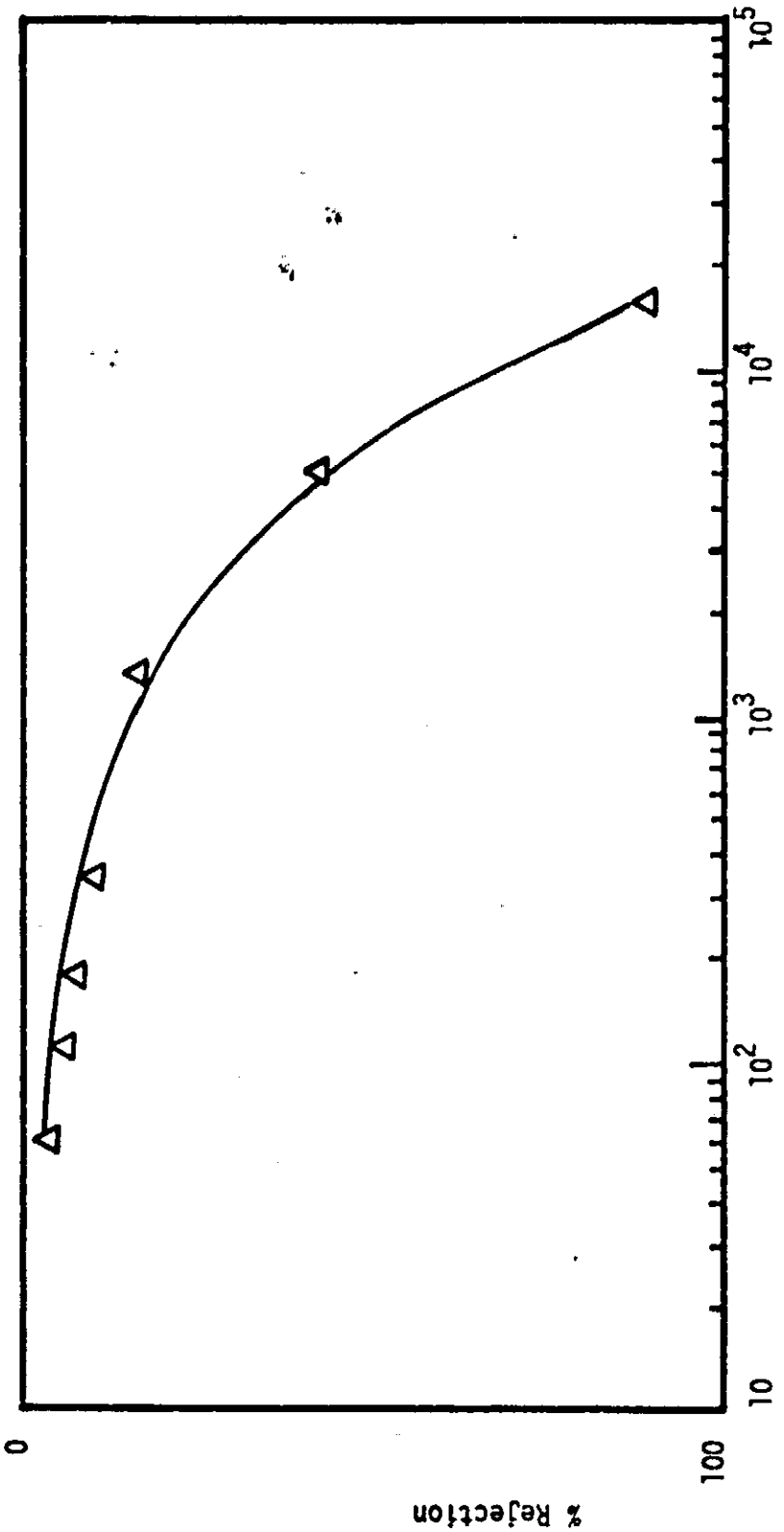

Figure 2. Rejection (%) as a Function of Test Solute Molecular Weight

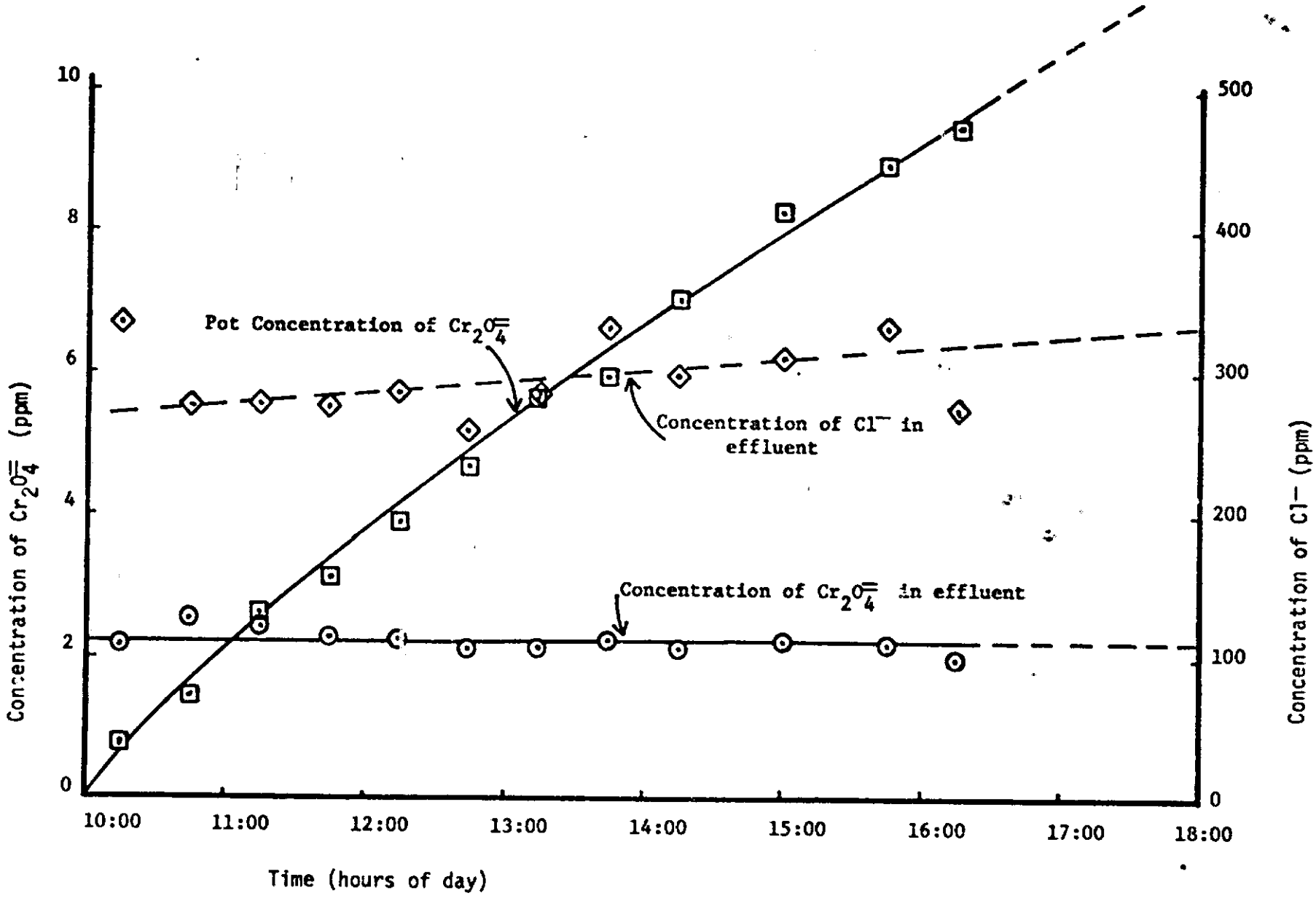

Figure 3. Dialysis of Chromate Through Ion Exchange Hollow Fiber. Feed concentration 10 ppm chromate. Flow rate 3.3 cc/min through 150 - 10-inch long fibers. Pot 3% NaCl.

SUMMARY

GSRI has produced hollow fibers which can be impregnated with an ion exchange resin. The untreated fiber can be manufactured in a reproducible manner with predictable properties. After-treatment of these fibers with polyvinylpyridine type resins produces an ion exchange fiber with excellent potential for application in Donnan dialysis. However, several problems remain to be resolved prior to any larger scale application:

1. An improvement is needed in the method of application to facilitate a continuous or more economical method of impregnation.

2. A more stable deposition of the impregnated resin is needed.

3. Studies are necessary to delineate whether a continuous deposition is required in the wall of the fiber or whether a surface deposition of a thinner film can achieve the desired results.

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