

## ZETA POTENTIAL CONTROL IN DECONTAMINATION WITH INORGANIC MEMBRANES AND INORGANIC ADSORBENTS

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### Abstract

The application of some advanced separation processes such as microfiltration and ultrafiltration, electroosmosis and electrodialysis for treating nuclear waste from different aqueous streams is under examination at the Chilean Commission for Nuclear Energy. The application of these techniques can be extended to regular industrial wastes when economically advisable. This report deals mainly with electrodialysis, electroosmosis and adsorption with inorganic materials. Special attention is paid to zeta potential control as a driving factor to electroosmosis. For radioactive contaminants that are present in the form of cations, anions, non-ionic solutions, colloids and suspended matter, appropriate combination of the processes may considerably increase the efficiency of processes used. As an example, colloids and suspended particles may be retained in porous ceramic membranes by nanofiltration, ultrafiltration or microfiltration depending on the particle size of the particles. The control of zeta potential by acting in the solid phase or else on the liquid phase has been studied; a mathematical model to predict electrodialysis data has been developed, and finally, the use of a home-made inorganic adsorbent illustrated. The effect of gamma irradiation on the membranes has also been studied. Properties such as salt retention, water flux and pore size diameter determined on both organic and inorganic membranes before and after irradiation indicate deterioration of the organic membrane.

### 1. INORGANIC MEMBRANES

Inorganic membranes are more stable in the presence of ionizing radiation making them particularly suitable for use for decontamination of radioactive waste. Inorganic membranes also show wider operational range of pH and temperature. Figure 1 shows the pore size distribution of an inorganic membrane MK-40. It can be seen how pore size increases after irradiation at 7.5 MRads. After irradiation, this and other organic membranes do not transfer ions so well as before irradiation. On the contrary, inorganic membrane BPS transfer ions just as well as before irradiation with the same dose.

#### 1.1. MANUFACTURE AND CHARACTERIZATION OF INORGANIC MEMBRANES

The procedure to manufacture the support is illustrated in Fig. 2 and the procedure to manufacture the membranes, in Fig. 3. The manufacture of an inorganic membrane is based on two feed solutions that are placed at each side of a suitable support in order to react to form a precipitate with appropriate characteristics. For the membrane called BPS-20, the two solutions, called L (left - side) and R (right - side), are the following:

- L: 0.1 M barium chloride;
- R: 0.1 M sodium orthophosphate with 0.2 M sodium silicate.

For a membrane called BPS-11, two solutions are:

- L: 0.1 M barium chloride with 0.1 M sodium silicate
- R: 0.1 M sodium orthophosphate with 0.1 M sodium silicate.

Membranes are made by placing the defined feed solutions L and R at the corresponding side of the selected support and allowing the precipitate to form on both faces of the support previously fitted between two semi-cells. Fig. 4 shows the experimental arrangement of the cells and membranes. This arrangement is utilized both for manufacture of the membrane as well as for the electrodialysis runs. While manufacturing the membrane, no external field needs to be applied.

In order to optimize the fixation of the membrane precipitate on the support, chemical precipitation is followed by electro-precipitation using the same feed solutions and external voltage applied ca. 10 V for three hours, after which the both solutions and the voltage are reversed for the same period of time. With this procedure the film formed on the support has better properties, and the reproducibility of results is assured.

In order to obtain a good inorganic membrane first it is necessary to have a well characterized support. In the previous work it was determined that the average pore size diameter needs to be within the range 0.3 to 2.5  $\mu$ . Outside this range, the membranes produced do not exhibit good properties because when the diameter is smaller, the penetration of the precipitate is not adequate, and when the diameter is larger, the precipitate does not adhere well to the support.

In the present work, the porous ceramic supports were made of alpha-alumina, A-5 and A-14, clays and diatoms (AD, 85% clay and 15% diatoms). Table I shows the properties of powders used to prepare the supports, some properties of the supports and of the membranes.

## 1.2. ELECTRODIALYSIS

Electrodialysis has been used for decontamination of some ionic radioactive solutions. This process is based on electromigration of ions through a membrane that permits the passage of ions of positive or negative charge. Inorganic membranes are not specific ion exchangers, to a large extent their exchange properties depend on the pH of the solution; being anion exchangers at low pH and cation exchangers at high pH. Figure 5 illustrates the reactions taking place in the electro dialysis cell and at each electrode. The experimental runs were carried out using a solution of 500 or 1000 parts per million  $Sr^{2+}$  (in nitrate form) as electrolyte. This concentration was chosen for a practical purpose. Typical radioactive wastes would have much lower concentration, in the order of a few parts per million or a few parts per billion prior to being concentrated.

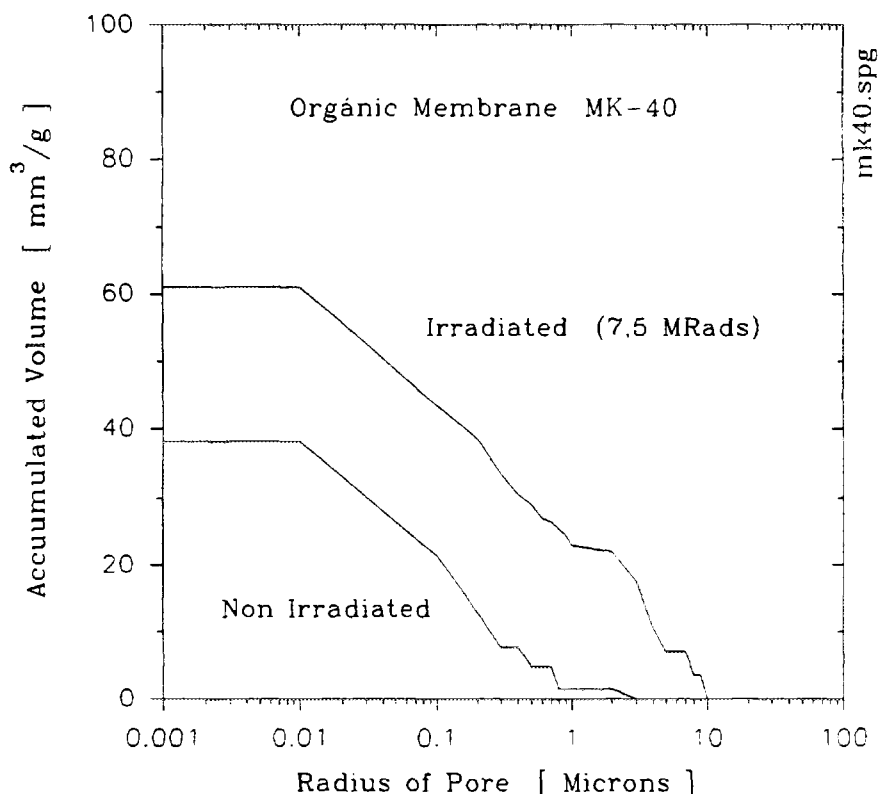
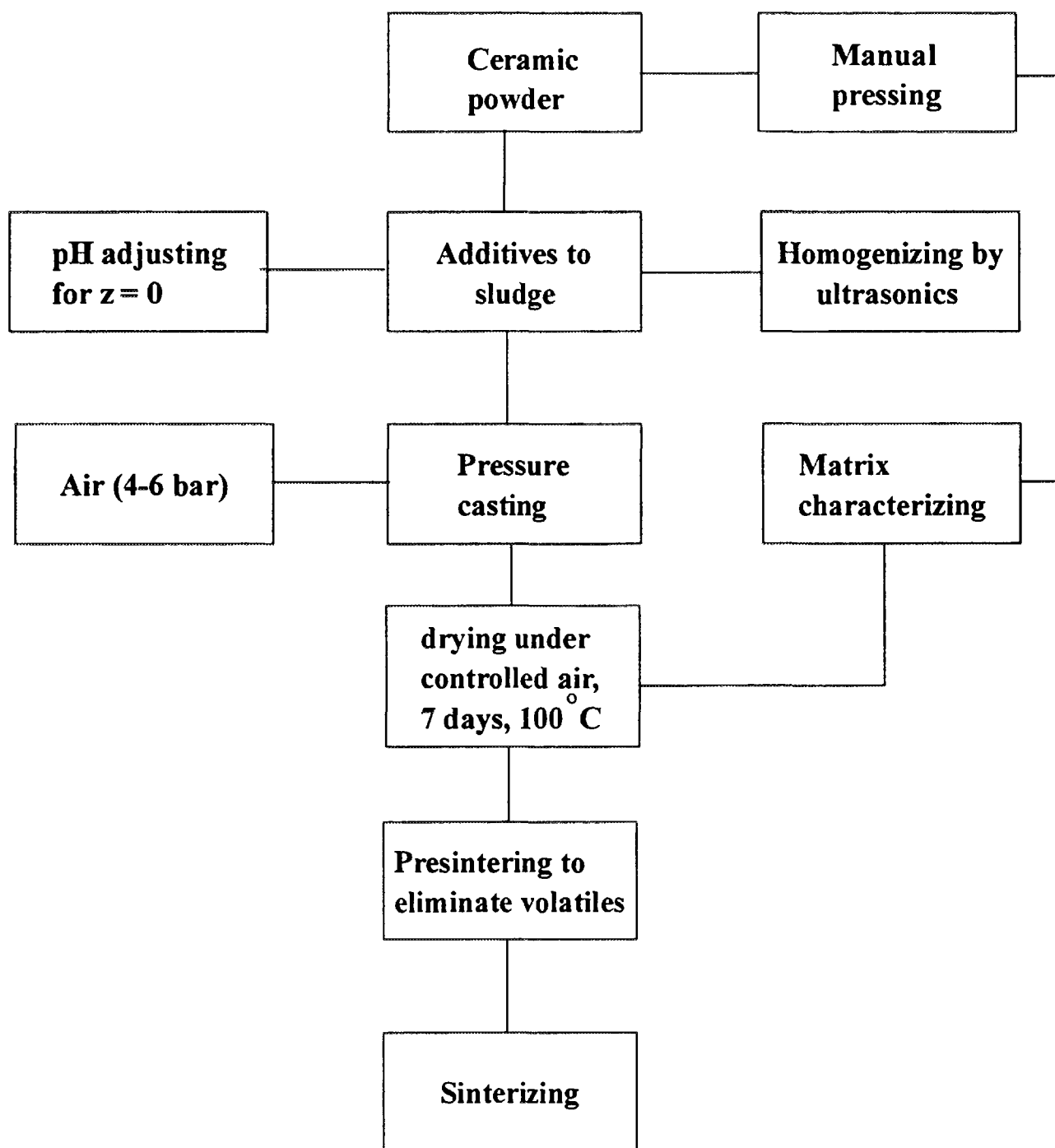
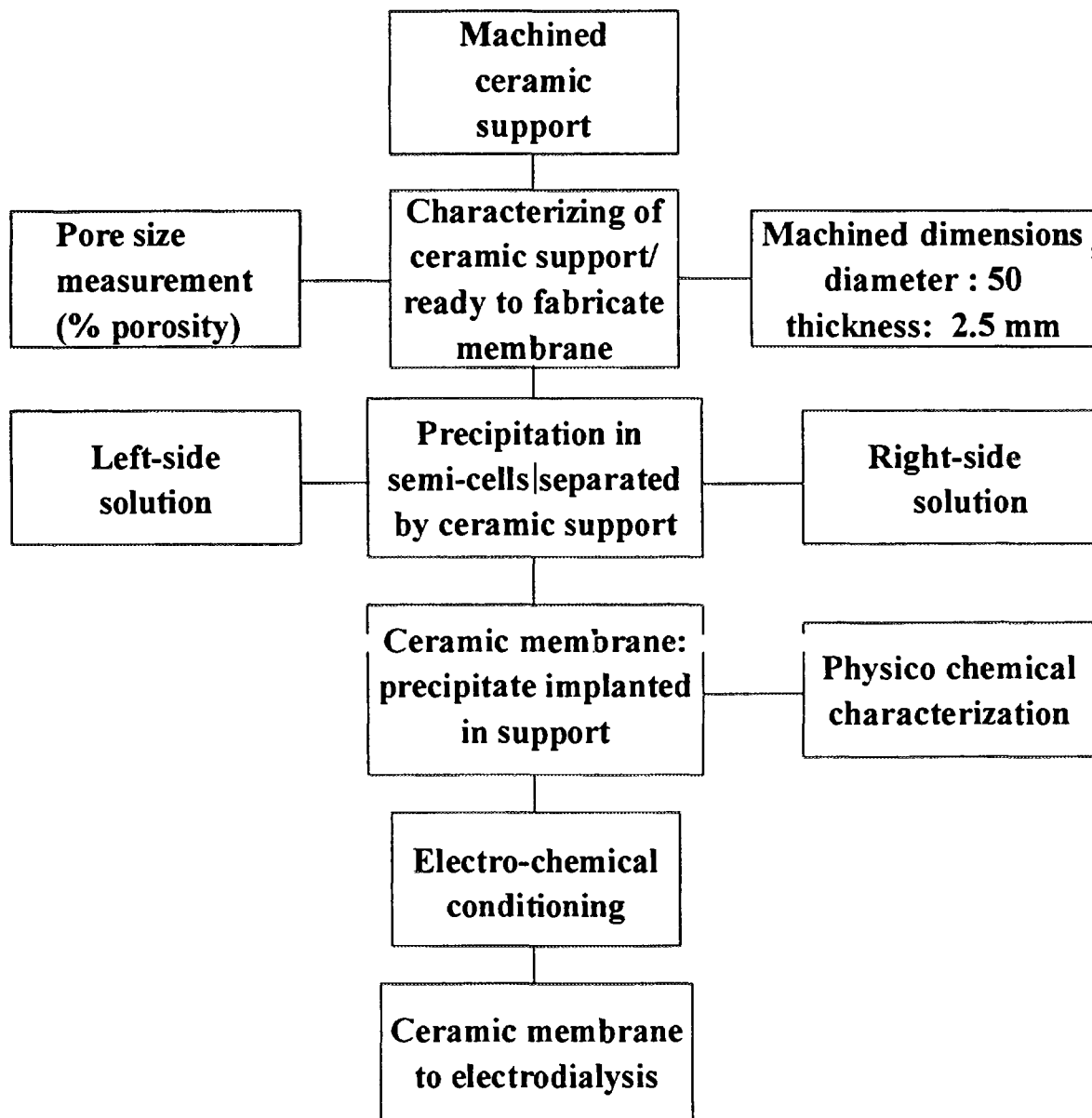


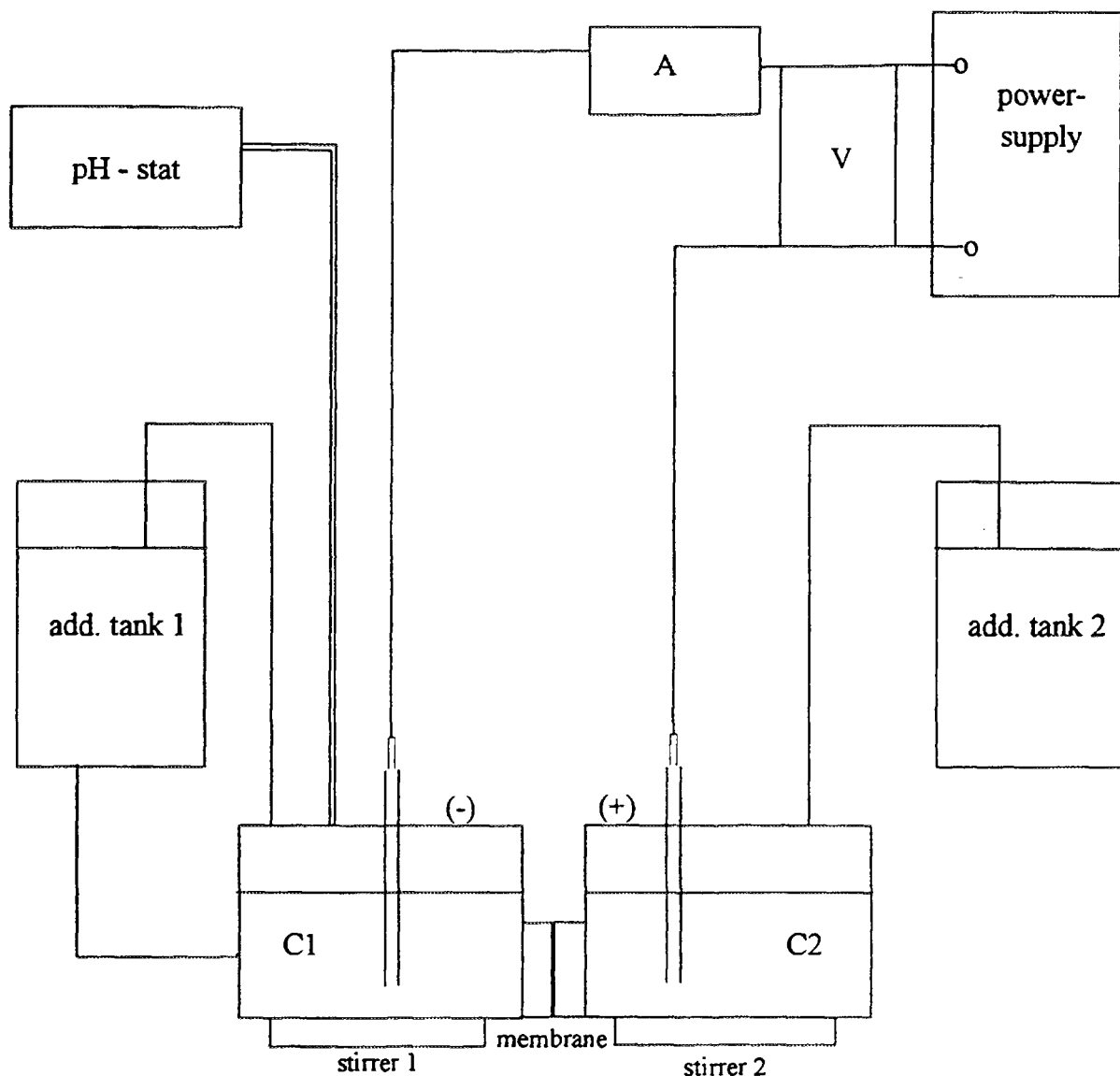
FIG. 1. Pore size distribution for an organic membrane MK-40 before and after irradiation at 7.5 MRads.



*FIG. 2. Fabrication of a ceramic support.*



*FIG. 3. Fabrication of an inorganic membrane.*



A = ammeter  
 V = voltmeter  
 C1, C2 = cathode, anode semicell  
 add. tank 1, 2 = additional tanks  
 (-) = cathode  
 (+) = anode

FIG. 4. Arrangement of the equipment for electrodiolysis.

TABLE I. CHARACTERIZATION OF POWDERS, SUPPORTS AND CERAMIC MEMBRANES

| Membrane                                   | Al-14 | Al-54 | Al-56 | AV     | AD     | Diatoms  |
|--|-------|-------|-------|--------|--------|----------|
| <b>1. Ingredients</b>                      |       |       |       |        |        |          |
| Alumina (%)                                | 99.6  | 99.2  | 99.2  | 28.0   | 24.1   | 2        |
| Silica (%)                                 | 0.08  | 0.02  | 0.02  | 50.8   | 57.9   | 98       |
| Average grain size ( $\mu$ )               | 2-5   | 6-10  | 6-10  | 0.1    | 1      | 12       |
| Ligand                                     | HMC   | HMC   | HMC   | -      | -      | Natrosol |
| <b>2. Conditions</b>                       |       |       |       |        |        |          |
| pH @ Z potential=0                         | 7.8   | 7.5   | 7.5   | -      | -      | -        |
| Packing pressure (bar)                     | 4     | 4     | 6     | manual | manual | manual   |
| Sintering temp. ( $^{\circ}$ C)            | 1600  | 1600  | 1600  | 950    | 1000   | 1150     |
| <b>3. Support</b>                          |       |       |       |        |        |          |
| Average pore size ( $\mu$ )                | 2.5   | 2.4   | 2.4   | 0.3    | 0.3    | 3        |
| Porosity (%)                               | 55    | 51    | 51    | 45     | 39     | 50       |
| Permeability (*)                           | 1000  | 1400  | 700   | 16     | 8      | 3200     |
| Limit of compression (kg/cm <sup>2</sup> ) | 620   | 89    | 338   | 715    | 530    | 36       |
| <b>4. Membrane BPS</b>                     |       |       |       |        |        |          |
| Average pore size ( $\mu$ )                | 1.7   | 2.3   | 2.3   | 0.15   | 0.21   | 2.5      |
| Porosity (%)                               | 48    | 45    | 48    | 33     | 38     | 47       |
| Permeability (*)                           | 220   | 100   | 80    | 5      | 4      | 2400     |
| Percentage of precipitate (**)             | 74    | 93    | 79    | 63     | 53     | 90       |

Key to symbols:

Al = Alumina

AV = Clay

AD = 85% clay, 15% diatoms

HMC = Hydroxymethylcellulose

(\*) = Permeability with respect to air in [cm<sup>3</sup>/min·cm<sup>2</sup>·bar]

(\*\*) = Ratio of precipitate implanted in open pore volume in %.

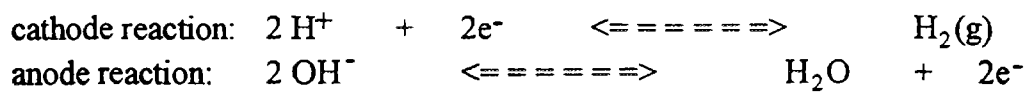
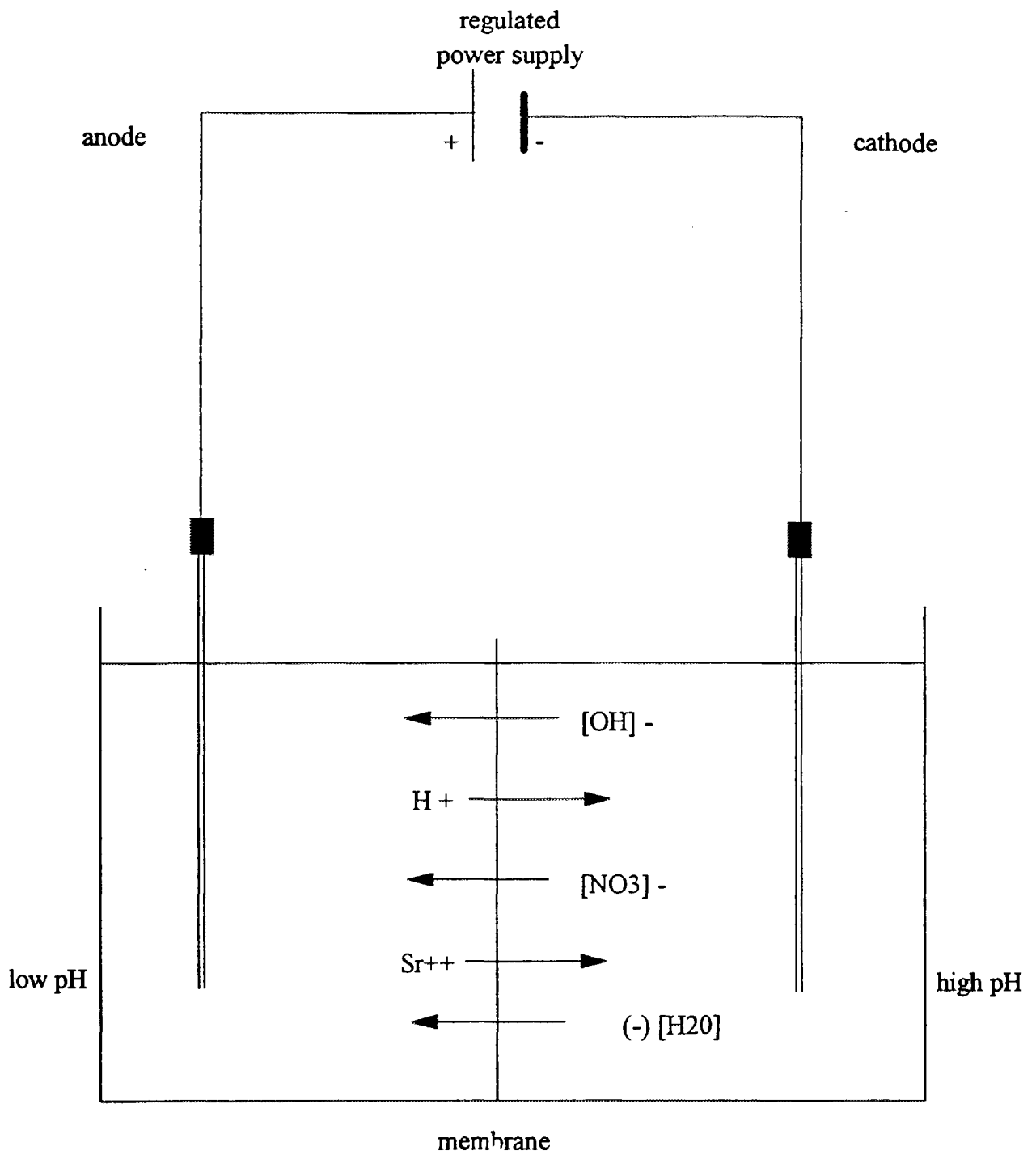


FIG. 5. Ions and water transfer in an electrodedialysis cell.

### 1.3. ELECTROOSMOSIS

Inorganic membranes are made in a hydrophilic medium where two precipitating solutions are placed at each side of a thin support form, so as to have precipitation to occur inside the support material. Organic membranes are produced in a hydrophobic environment, and water cannot flow as freely as in the case of inorganic membranes. In fact, inorganic membranes show distinct behavior with water. Water flows through the membrane in large amounts during electro dialysis. Figure 6 shows the transfer of very large amounts of water for the membrane BPS supported on the paper Whatman-50. This water flows through by several mechanisms adding together their individual contributions towards the total water transfer; simple osmosis being the least important.

### 1.4. ZETA POTENTIAL CONTROL

The transfer of water from one semicell to another in electro dialysis may be an undesirable feature of inorganic membranes since it is energy consuming and also the flow of water may go in the wrong direction. An important objective of this investigation is to control the degree of electroosmosis taking place in electro dialysis. This study would seek to manipulate the conditions that determine the value of zeta potential of the membrane as the main governing factor to this phenomenon. Figure 7 shows the dependency of the Zeta Potential from pH. The maximum difference of 60 mV was found between pH 2 and 11.

#### 1.4.1. Control in the solid phase

This part of the study is concerned with the support matrix inside which the membrane is formed and nested. Cellulose is the support material which shows very large electroosmotic ability. Using the ceramic support prepared by adjusting the zeta potential to value zero, shows important reduction of electroosmosis. Figure 8 shows a marked difference between a paper support and ceramic support, same as in Fig. 6, but this figure also shows the higher current consumption of the paper membrane due to water transport. Figure 9 shows that together with the lower power consumption the ceramic support can also be a better membrane than AD-3 and AD-2 for the transport of strontium.

#### 1.4.2. Control in the liquid phase

The other part of this study is concerned with the liquid phase by controlling such properties as pH, current density, addition of specific ions. A marked reduction in electroosmosis is attained by controlling pH at constant current. The pH control is not easily achieved. Figure 10 shows how pH naturally takes extreme values as soon as the electric field is applied.

The main purpose of the present study is to review the results of the actions taken to gain control of the zeta potential as the main driving force for the total amount of water to be transferred by electroosmosis in electro dialysis with inorganic membranes.

In the earlier work we observed a similarity between the curve for the zeta potential and the volumes of water transferred over the same range of pH in the solution. The work reported here was originated by this observation. It was decided to fix pH at several values in the range 1 to 14, keeping the current at a constant value to eliminate its influence. As a greater current is passed at the same pH value, more water is transferred because more faradays charge is passed. Keeping the current constant, the influence only of pH on the electroosmotic effect would be demonstrated.

For the control of pH, either 1M HNO<sub>3</sub> or 1M KOH is added as required. The amounts added, even though very small, are considered in the volume calculations. In all these runs, barium phospho-silicate membrane (BPS-20) supported in Whatman paper type 50 was used.

Figures 11 and 12 summarize the results obtained. These figures are two different ways of showing the same data. Figure 11 shows that there is a trend to transfer less water at higher pH at each current density that was tested. Figure 12 shows a very high amount of water transferred per faraday. The results obtained are controversial because each faraday there appears to be transporting more than one g-mole (18 g of H<sub>2</sub>O). There are numbers well in excess of one hundred moles per faraday.



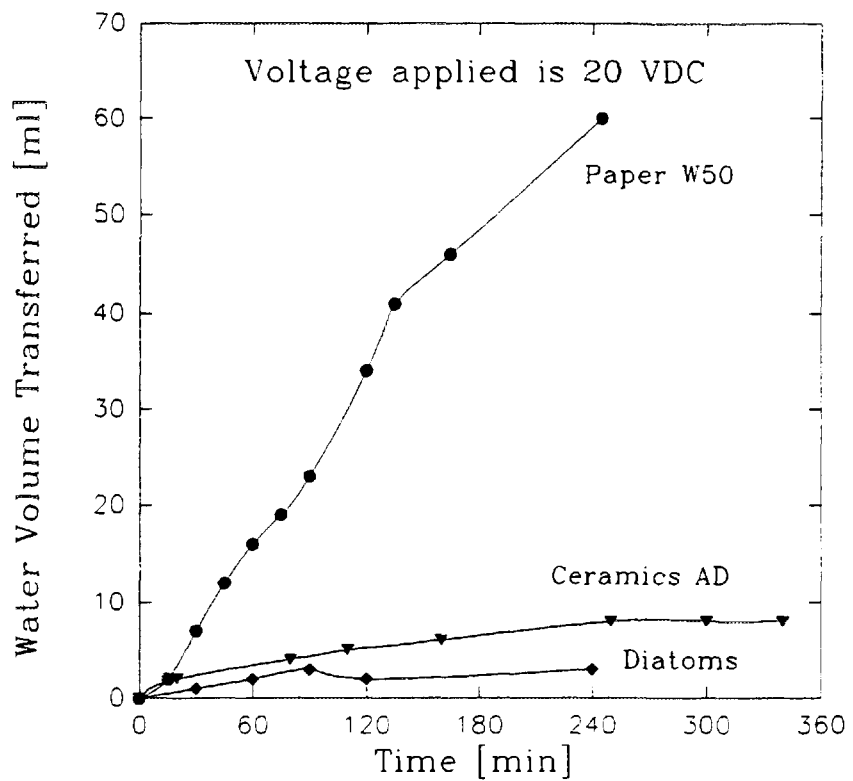


FIG. 6. Water volumes transferred by electroosmosis at 20V.

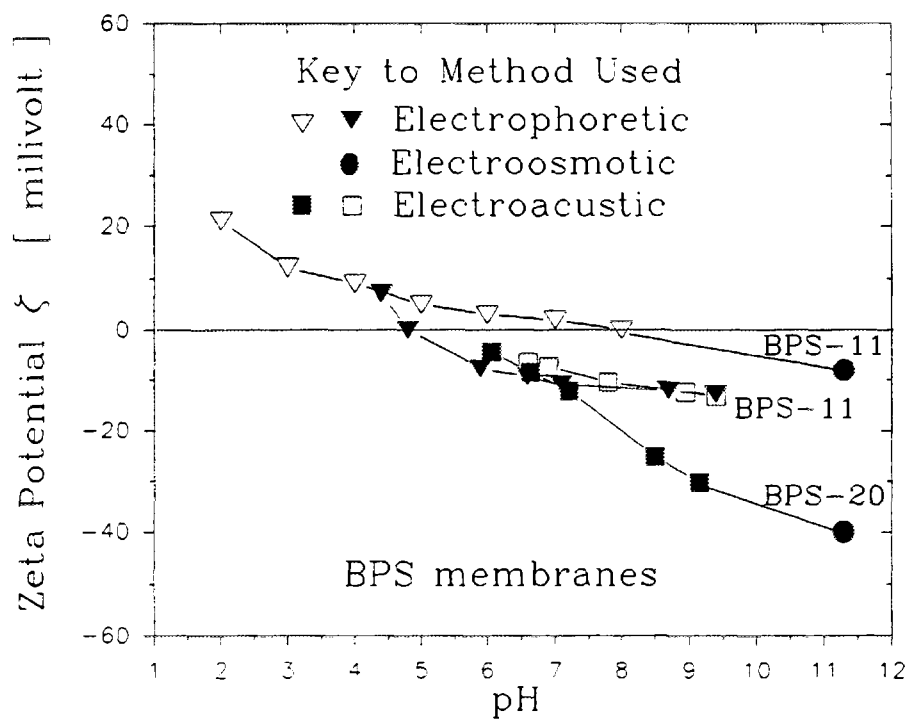


FIG. 7. Zeta potential for BPS membrane at pH2-7.

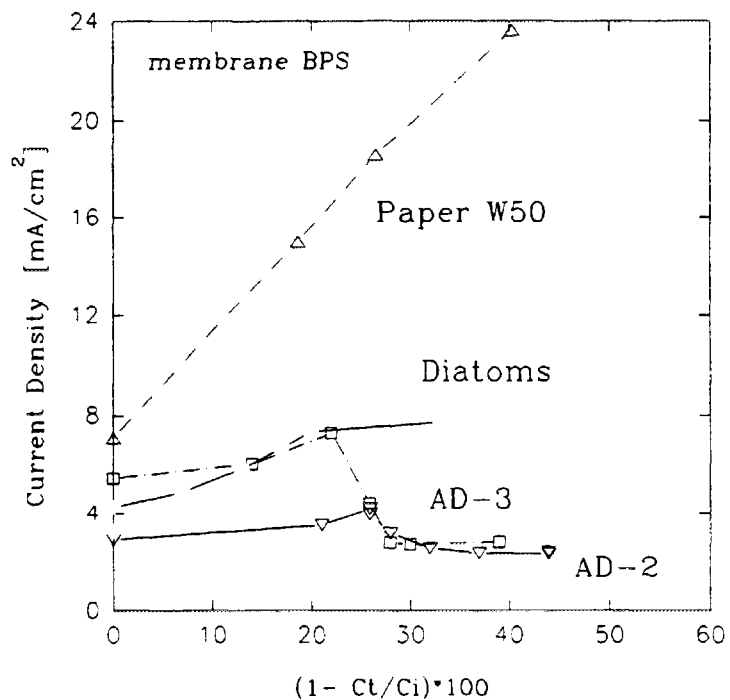


FIG. 8. Current density utilized to transfer ions with membrane BPS supported on several matrices

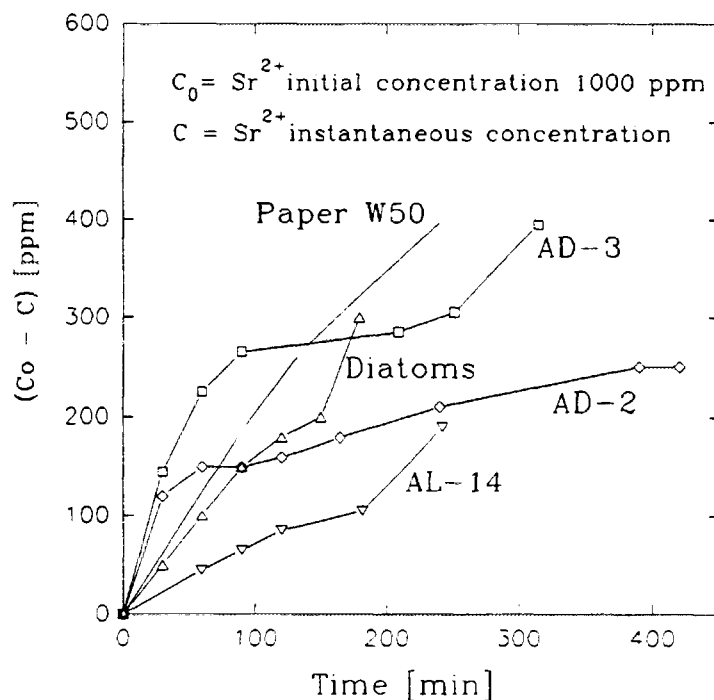


FIG. 9. Strontium transferred through membrane BPS supported by different matrices.

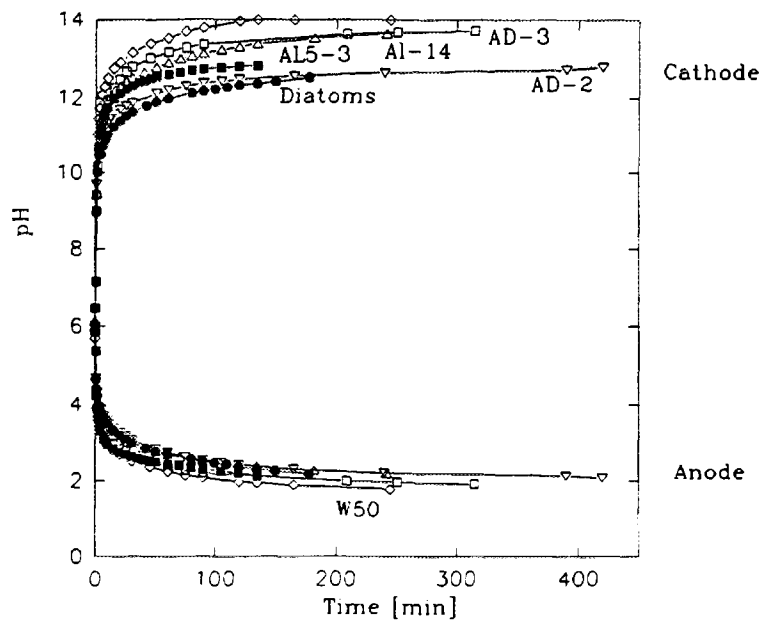


FIG. 10. Illustration of extreme separation of pH values for (high) cathode cell and (low) anode cell.

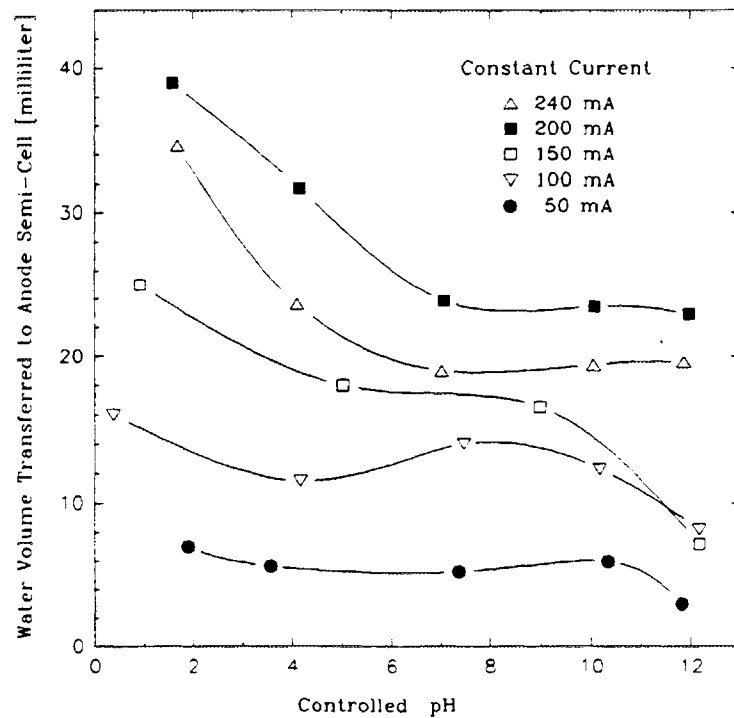


FIG. 11. Electroosmotic effect with an inorganic membrane BPS at constant currents of 50, 100, 150, 200 and 240 mA.

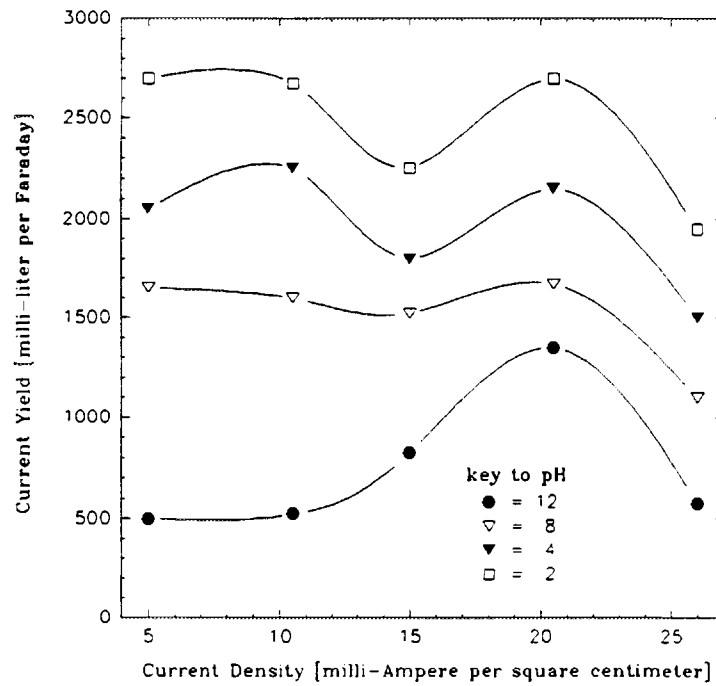


FIG. 12. Electroosmotic yield at different pH for the same current density.

## 2. MATHEMATICAL MODELING OF ELECTRODIALYSIS

The Nernst-Plank equation in the form presented by Goldman has been used to obtain the data needed to design a demonstration electrodialysis plant fitted with an inorganic porous membrane. The specific data needed in the model for each system are the membrane potential, the ionic mobility and the membrane thickness. This treatment falls in the realm of classical thermodynamics and is restricted to isothermal systems. Different treatment is advised to deal with organic membranes. Those can be treated as a series of barriers (corresponding loosely to the active centers). This treatment usually leads to an equation that requires data that are not available or too difficult or impossible to get. The resulting equations are too difficult to test experimentally.

The Nernst-Plank equation treats the flux  $J_j$  for ions  $j$  through the membrane in terms of the electrochemical potential. For ideal solutions, in a constant electric field inside the membrane, the equation known as the Goldman equation, is as follows:

$$J = - \frac{\alpha \mu RT (C_1 - C_n \exp\{\alpha\})}{d(1 - \exp\{\alpha\})} \quad (1)$$

where

$\mu$  is the ion mobility of species  $j$ ,  
 $d$  is the membrane thickness,  
and  $\alpha$ :

$$\alpha = \frac{zF\Delta\Psi}{RT} \quad (2)$$

where

z is the charge,  
 R is the gas constant,  
 T is the absolute temperature, and  
 $\Delta\Psi$  is the membrane potential.

From the theory of the absolute speed of reaction, a formula that is similar to Goldman equation can be obtained, if the factor  $K_1 \Lambda^2 / d$  with the ionic permeability  $\mu RT/d$  is identified:

$$J = - \frac{\alpha K_1 \Lambda^2 (C_1 - C_2 \exp\{\alpha\})}{d(1 - \exp\{\alpha\})} \quad (3)$$

This equation can be used for the isothermal systems with negligible pressure effects, and with an equal mean distance between potential barriers, and also with constant electric field. Next, the relation between the flux and the instantaneous concentration can be considered as:

$$J = - \frac{V}{A} \cdot \frac{dC}{dt} \quad (4)$$

where

V is the cell volume, and  
 A is the membrane surface area.

Also, since the volumes on each side of the membrane are equal, the following relation for the anode and cathode concentrations can be obtained:

$$C_2 = 2C_0 - C_1 \quad (5)$$

where

$C_0$  is the initial concentration,  
 $C_1$  is the anode concentration, and  
 $C_2$  is the cathode concentration.

If to equations (1) and (4) are equated, the resulting equation integrated, we will get, at a constant electric field:

$$C = \frac{C_0 \exp\left\{-\frac{\alpha A \mu RT (1 + \exp\{\alpha\})}{V d (1 - \exp\{\alpha\})} \cdot t\right\} + 2C_0 \exp\{\alpha\}}{1 + \exp\{\alpha\}} \quad (6)$$

This is the model equation sought. In order to test equation 6, values for the membrane potential  $\Delta\Psi$ , the ion mobility  $u$ , and the membrane thickness  $d$  (in order to calculate the ionic permeability,  $\mu RT/d$ ) need to be known.

## 2.1. ION MOBILITY

Ion mobility, " $\mu$ ", is the ion velocity under unit driving force, in this case, unit electric field. The ion mobility can be estimated from:

$$\mu = \frac{6.469 \cdot 10^6 \cdot \lambda}{z} \quad (7)$$

where

$\lambda$  is the electrolytic conductivity for the ion  $\text{Sr}^{2+}$ , its value is  $59.4 \text{ cm}^2 \Omega^{-1} \text{ g-eq}^{-1}$  at  $25^\circ \text{C}$ .

The ion mobility is then estimated at  $1.92 \cdot 10^{15} \text{ cm}^2 \text{ s}^{-1} \text{ J}^{-1}$ .

## 2.2. MEMBRANE THICKNESS

Membrane thickness can be estimated from:

$$d = \frac{4m}{\pi \rho D^2} \quad (8)$$

where

$m$  is the mass of membrane,  
 $\pi$  is 3.14159,  
 $\rho$  is the density of membrane, and  
 $D$  is the diameter of membrane.

The value obtained is  $2.235 \cdot 10^{-2} \text{ cm}$ .

## 2.3. MEMBRANE POTENTIAL

A membrane potential arises from the double layers formed on the membrane surface; or for porous membranes, inside pores. It can be measured in an arrangement such as :

solution 1 / membrane / solution 2

So that, the membrane potential  $\Delta\Psi = \Psi_2 - \Psi_1$ . This value was measured experimentally as 100 mV.

To obtain the numerical equation to be tested, the ionic permeability from the literature was estimated, the membrane thickness was calculated from the experimentally measured values. The other value needed, namely, the membrane potential was measured with standard electrodes each side of the membrane. The results are shown in Fig.13. The potential difference during about 60 minutes was measured, which is a time lapse of interest for the design. During this time the concentrations changed to 1.5 from the initial concentration. This value will be used to design the electrodialysis equipment. From the graph it can be seen that the potential difference remains almost constant at 100 mV. So this value was used. With all these values replaced in the equation, the following numerical equation can be finally obtained:

$$C = -0.96 \cdot C_0 \exp\left\{1.44 \cdot 10^{-3} \cdot \frac{A}{V} \cdot t\right\} + 1.96 \cdot C_0 \quad (9)$$

with  $t$  in seconds and  $C$  in parts per million.

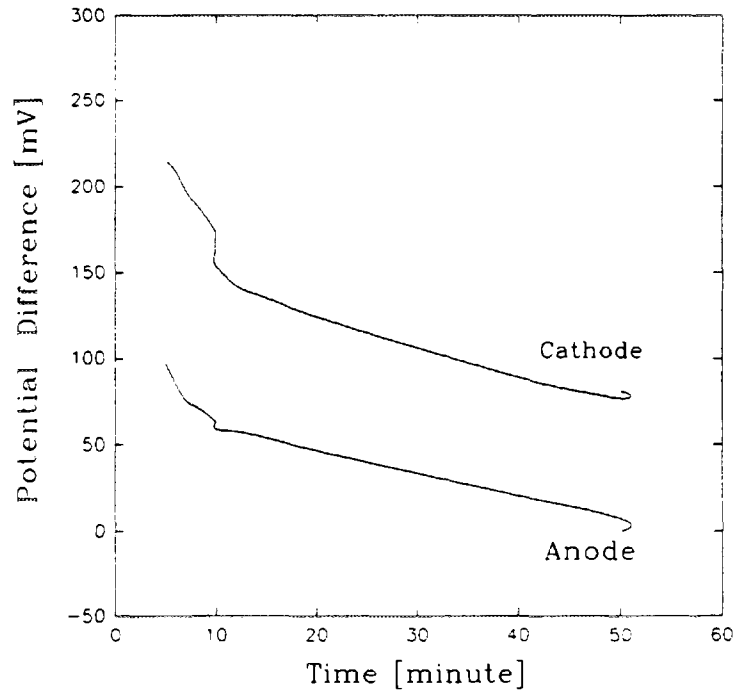


FIG. 13. Membrane potential for membrane BPS measured during the time lapse that will be used for testing the model equation and the design of the equipment.

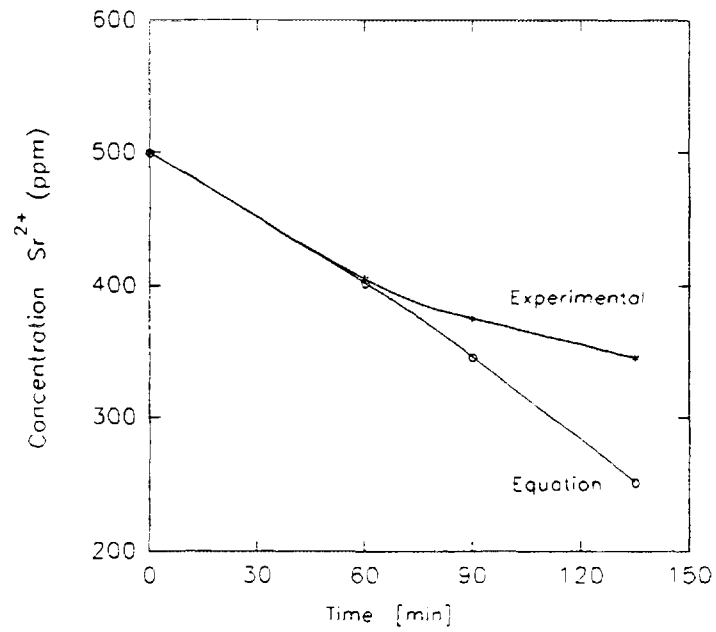


FIG. 14. Comparison of experimental data with the data produced by the model equation for starting concentration of 500 ppm.

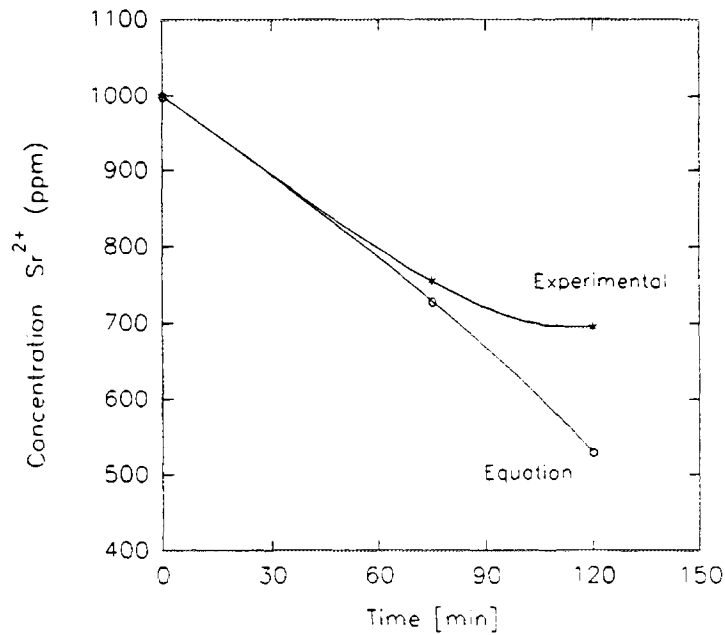


FIG. 15. Comparison of experimental data with the data produced by the model equation for starting concentration of 1000 ppm.

Figures 14 and 15 show the results of comparison of experimental data with the model equation. These two figures show that the model equation reproduces well the experimental data for up to 60 minutes. This is enough time for design purposes.

### 3. THE USE OF INORGANIC ADSORBENTS

Homemade  $\text{MnO}_2 \cdot \text{SiO}_2$  has been used to further decontaminate the final dilute effluent (permeate). Adsorbents may be of organic or inorganic nature. Organic materials known to be unstable at high levels of radiation, may be deformed at moderate temperatures and are not recommended for encapsulation in concrete. On the other hand, inorganic adsorbents are stable at high temperatures, may withstand higher levels of radiation and are more selective. Many inorganic materials have been tested, but here only one composite that is very easily manufactured and shows good results is described:  $\text{MnO}_2 \cdot \text{SiO}_2$ . Adsorbent  $\text{MnO}_2 \cdot \text{SiO}_2$  was prepared by reduction of  $\text{KMnO}_4$  in the presence of sodium silicate at a basic pH.

Representative results for the stripping of electro dialysis permeates are shown in Table II, as decontamination factors and distribution coefficients. In the three cases shown, the decontamination factor was better than 98%.

A property to compare the performance of adsorbents is the distribution coefficient that is calculated as follows:

$$K_d = \frac{(C_i - C_f) \cdot V}{C_f \cdot W} \quad (10)$$



TABLE II. DECONTAMINATION PERCENTAGE AND DISTRIBUTION COEFFICIENTS

| Silica (%) | pH   | Size ( $\mu$ )  | Decontamination | Distribution coefficients |
|------------|------|-----------------|-----------------|---------------------------|
| 10         | 5.8  | less than 75    | 98.7 %          | 15500                     |
| 17         | 10.9 | between 250-420 | 98.2 %          | 11400                     |
| 24         | 10.9 | less than 75    | 98.5 %          | 13800                     |

#### 4. CONCLUSIONS

The use of inorganic materials, namely, inorganic membranes and inorganic adsorbents for treatment of radioactive waste is based on the fact that organic membranes have shown signs of deterioration when submitted to intense gamma radiation. So these inorganic materials should be preferred in the presence of high radiation fields. Inorganic materials are better from the standpoint of secondary waste to be immobilized for final disposal, and they also show a wider operational range with regard to pH and temperature.

These techniques have other advantages: they generate minimum amount of secondary waste, operate under mild conditions and have good process control variables. On the other hand, these techniques do not avoid some deficiencies. From one side, inorganic membranes do show a strong electroosmotic effect, in transferring large volumes of water to one electrode cell. This effect can be detrimental to the process. If the control of both the volume transferred and the direction of the electroosmotic flux is provided, this effect can be avoided and may be considered, as a desirable property. Recently it became known as electroosmotic dewatering.

##### 4.1. ZETA POTENTIAL CONTROL

The results obtained confirmed the initial hypothesis as reported in the earlier work, that higher the pH, the lower the electroosmotic effect for the same current density. (It is of interest to study the number of moles of water transferred per faraday, in relation to the structure of water, for instance).

##### 4.2. MATHEMATICAL MODEL

The electro dialysis model equation represents satisfactory the data for a reaction time up to 60 minutes.

##### 4.3. INORGANIC ADSORBENT

The home-made inorganic adsorbent  $MnO_2 \cdot SiO_2$  can effectively strip the electro dialysis tailings, leaving less than 1 ppm in the supernatant liquid.

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