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Strontium Separation with Ultrafiltration Membranes from Dilute Aqueous Solutions

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Abstract

The separation of Sr^{2+} from dilute and trace solutions of low activity by means of hollow fiber Amicon ultrafiltration membranes is studied. The cation is absorbed on colloidal particles of titanium oxide formed directly in solution, and the colloidal dispersion is filtrated. The method has been studied under several different operative conditions (pH, Ti/Sr ratio, the presence of interfering ions, colloid formation time) with the aim of determining the optimum conditions to develop a separation process.

INTRODUCTION

The use of ultrafiltration to separate metal ions from dilute solutions is a very promising method for the treatment of liquid nuclear and conventional wastes (*1, 2*). Metal ions in solution are bound by adsorption or complexation to soluble macromolecules, emulsion droplets, or colloid particles. The resultant solution or dispersion is ultrafiltrated through a membrane of selected cut-off (*3*). The metal ion is concentrated in the retentate.

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In this work the separation of Sr^{2+} adsorbed on colloidal titanium hydroxide is studied. Three different aqueous solutions are considered: (a) a dilute nonradioactive aqueous $Sr(NO_3)_2$ solution used to select operating conditions, (b) a low activity solution corresponding to the water of the storage pond of Magnox-type fuel elements (exhausted or damaged) (pond solution P), and (c) tail-end solutions of the decontamination process of the storage pond water (S11 solutions). These last two solutions were obtained from the ENEL power plant of Latina, Italy.

EXPERIMENTAL

Inactive Dilute Strontium, $Sr(NO_3)_2$, Solutions

Titanium or in some experiments zirconium colloidal hydroxides were formed in $Sr(NO_3)_2$ solutions from the chloride salts by varying the pH with NaOH (final pH > 8). Carlo Erba purity grade reagents were used as received. The colloid suspension was left in contact with the aqueous solution for 2–3 h and then was ultrafiltrated. Amicon hollow fiber cartridges H1P5 with 0.06 m^2 membrane area were operated with a DC2 Amicon device at 1.2 atm pressure. Membranes were polysulfone asymmetric fibers with 5000 MW cut-off. A volume of 2000 cm^3 of feed solution was circulated at 600 cm^3/min. The separation was stopped when the initial volume was reduced to 100 cm^3. Strontium analysis in the concentrate and permeate solutions were made by flame photometry with a Perkin-Elmer 5000 atomic adsorption spectrophotometer. The experimental arrangement for the separation test is shown schematically in Fig. 1 as an ultrafiltration process at low pressure with recycling of the rejected stream. Low pressure is imposed both by the mechanical hollow fiber resistance and for the purpose of reducing the sticking of colloid particles on the fiber walls. No prefilter was used in this set of experiments.

Low Activity Solutions

The composition and physical chemical properties of these P and S11 solutions are reported in Table 1. ^{90}Sr was added together with inactive Sr to the feed solution (2000 cm^3) up to a concentration of 5 ppm. Inactive

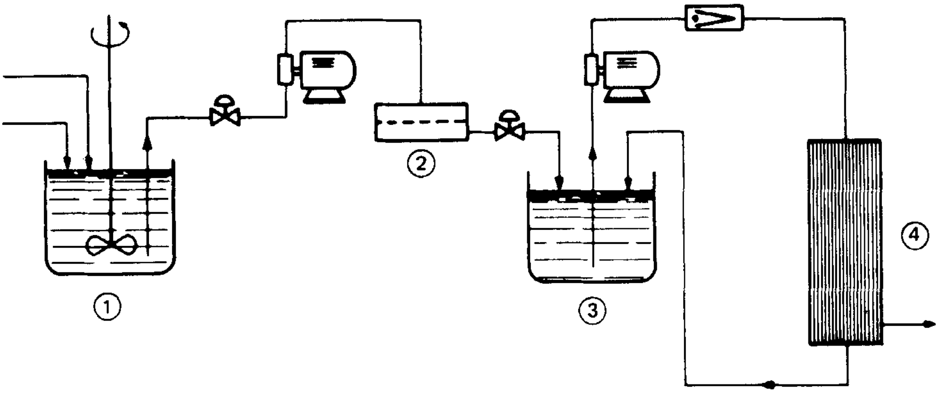

FIG. 1. Schematic diagram of the filtration process: (1) reactor for the colloid adsorption, (2) prefilter (Millipore 0.45 or 0.2 µm, (3) feed collection tank, (4) Amicon hollow fiber membrane module.

TABLE 1

Chemical Composition and Physical Chemical Properties of the P and S11 Radioactive Solutions from a Magnox-type Fuel Storage Pond and the Pond Water Decontamination Process

	Storage pond P solution	Tail-end S11 solution
Chemical composition ($\mu C_i/L$):		
^{90}Sr	2.2	3×10^{-1}
$^{134+137}Cs$	50.0	5×10^{-2}
^{144}Ce	10.0	5×10^{-3}
^{51}Cr	1.0×10^{-1}	
^{106}Ru	3.0	3×10^{-3}
$^{95}Nb + ^{95}Zr$	5.0	2×10^{-3}
^{60}Co	—	3×10^{-4}
^{45}Ca	1.2	—
^{35}S	2.0×10^{-1}	—
^{35}Ca	3.0×10^{-1}	—
Physical chemical properties:		
Temperature, °C	29–30	—
Conductance, µS	1300	—
pH	11.5	8–9
Na_2CO_3, ppm	250	—
$NaNO_3$, %	—	3–4
Chloride ions, ppm	0.35	—
NaOH, ppm	110	—

strontium acts as a carrier for the isotope. The $Ti(OH)_4$ colloid was formed from $TiCl_4$ by adding NaOH (pH = 10 or 12). The Ti/Sr equivalent ratio was generally fixed at 2/1. The experimental separation test was the same as reported in Fig. 1 but a prefiltration step with Millipore membranes of 0.45 or 0.2 μm average pore diameter was inserted. The efficiency of the ultrafiltration process was tested on the permeate by measuring the decontamination factor, DF, i.e., the ratio between the feed and the permeate activities. The activity was measured with a solid scintillator (organic crystal) after Sr isotope separation with 75% HNO_3. The initial feed volume was reduced to 100 cm^3.

During experiments with inactive and low activity solutions, fluxes across the membrane cartridge remain practically constant, at least during the 2–3 h needed to obtain the wanted volume reduction. This is shown in Fig. 2 where the feed volume decrease in some typical separation runs is reported against time. Corresponding volume fluxes fall in the range 15–20 cm^3/min. These small values are essentially due to the available surface membrane area in DC2 Amicon modules, and they can easily be enhanced by a factor of 20 by using large modules. In this case the volume fluxes will be more meaningful for a real process evaluation.

RESULTS AND DISCUSSION

The point of zero charge for TiO_2 in an electrolyte solution ($NaNO_3$) is found at pH = 6.5 (*4*). At higher pH the hydrated oxide shows a negative surface charge which is reversed when alkaline-earth cations are specifically adsorbed (*4*). At pH $\simeq$ 10 in $Sr(NO_3)_2$ 1.67×10^{-5} *M* solutions, the titanium hydroxide colloid is positively charged. As a consequence, titanium hydroxide colloid is a cation exchanger at high pH and an anion exchanger at low pH (*5, 6*). The exchange capacity of the colloid strongly depends on the preparation method and the chemical environment. However, the adsorption rate is always low and full equilibrium between colloid and solution is reached after 2–3 weeks for elements in solution at a very low concentration (*5, 6*). Therefore, under the experimental conditions of the separation tests of this work, equilibrium is not attained before filtration.

The order of interaction for alkaline-earth cations with titanium hydroxide particles, at a given metal concentration, is (*4*) Ba $\gg$ Sr >

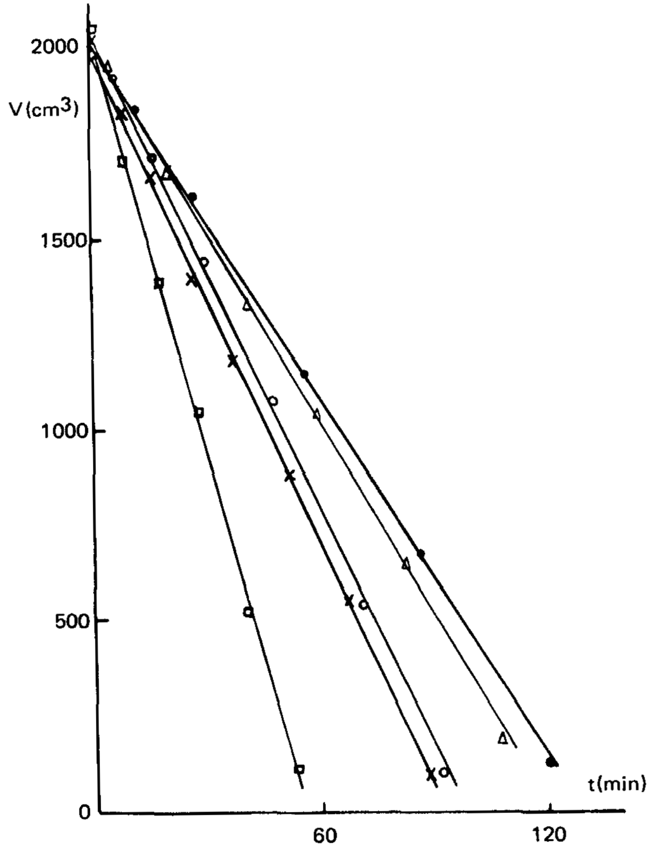

FIG. 2. Volume decrease of the feed solution during separation tests: (●) Ti/Sr = 1/1, pH = 10; (×) Ti/Sr = 2/1, pH = 8; (△) Ti/Sr = 2/1, pH = 10; (○) Ti/Sr = 2/1, pH = 12; (□) Ti/Sr = 2/1, Mg/Sr = 2/1, pH = 10.

Ca > Mg. The interaction mechanism can be written

$$\mathrm{TiOH} + \mathrm{OH^-} \rightleftharpoons \mathrm{TiO^-} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{TiO^-} + \mathrm{Sr^{2+}} \rightleftharpoons \mathrm{TiOSr^+} \tag{2}$$

since the ion-exchange sites at the surface of crystallites are assumed to be the $-\mathrm{OH}$ terminal groups (*5*). This simplified picture represents the basis of the proposed separation method.

To assess the conditions for the best distribution of Sr^{2+} between solution and titanium hydroxide colloid particles, kinetic tests have been performed in batch conditions. At a given pH and Ti/Sr ratio, the concentration of Sr in the feed solution (typically a 5-ppm Sr solution) and the amount adsorbed on colloid particles were measured as a function of time. The Sr distribution between the solution and the colloid phases was determined by collecting aliquots of the colloidal dispersion (10 cm^3) at different times. The liquid phase was separated by centrifugation and filtration and analyzed for the Sr in solution. The precipitate was rapidly washed with an alkaline solution and then dissolved to measure the Ti and Sr content. The data so obtained and the calculated concentration factors and distribution coefficient for Sr ions are collected in Table 2. The reported values represent data after 6 h of equilibration.

TABLE 2
Concentration Factors for Sr in Titanium Colloid Particles. Initial Solution: 5 ppm in Sr

	pH		
	8	11	12
Ti/Sr = 1:			
Sr^{2+} solution (ppm)	1.60	0.84	0.39
Ti/Sr molar ratio (colloid)	—	2.19	1.98
% Initial Sr (colloid)	68.0	83.2	92.2
$\left(\dfrac{\text{Sr in colloid, mg/g Ti}}{\text{Sr in solution, mg}} \times 10^{-3}\right)$	—	0.99	2.36
Ti/Sr = 2:			
Sr^{2+} solution (ppm)	0.55	0.26	0.05
Ti/Sr molar ratio (colloid)	—	3.86	3.70
% Initial Sr (colloid)	89.0	94.8	99.0
$\left(\dfrac{\text{Sr in colloid, mg/g Ti}}{\text{Sr in solution, mg}} \times 10^{-3}\right)$	—	1.82	9.90
Ti/Sr = 4:			
Sr^{2+} solution (ppm)	0.32	0.09	0.03
Ti/Sr molar ratio (colloid)	—	7.45	7.35
% Initial Sr (colloid)	93.6	98.2	99.4
$\left(\dfrac{\text{Sr in colloid, mg/g Ti}}{\text{Sr in solution, mg}} \times 10^{-3}\right)$	—	2.73	8.28

However, the same results were obtained with samples collected after 15 min of equilibration. A typical curve is shown in Fig. 3. Effective equilibrium was not reached because that would take a much longer time than the duration of the experimental separation test (*5*). For this reason and because the colloid surface area is not known, the adsorption isotherm parameters and the equilibrium constant for the Sr colloid interaction do not appear in Table 2; only concentration factors and Sr distribution between colloid and solution are reported.

As a partial conclusion it may be said that the colloid particles are practically saturated after a few minutes and the best conditions for particles loading in Sr solutions correspond to pH 11–12 and a Ti/Sr ratio between 2 and 4. To test these conclusions, the separation efficiency for Sr cation following the proposed method was tested in $Sr(NO_3)_2$ dilute solutions (typically 5 ppm) measured at different pH and Ti/Sr ratios of both the retentate and permeate solution concentrations as a function of time. The retention curves show (Fig. 4) that during the ultrafiltration step both retentate and permeate concentrations decrease, especially at the

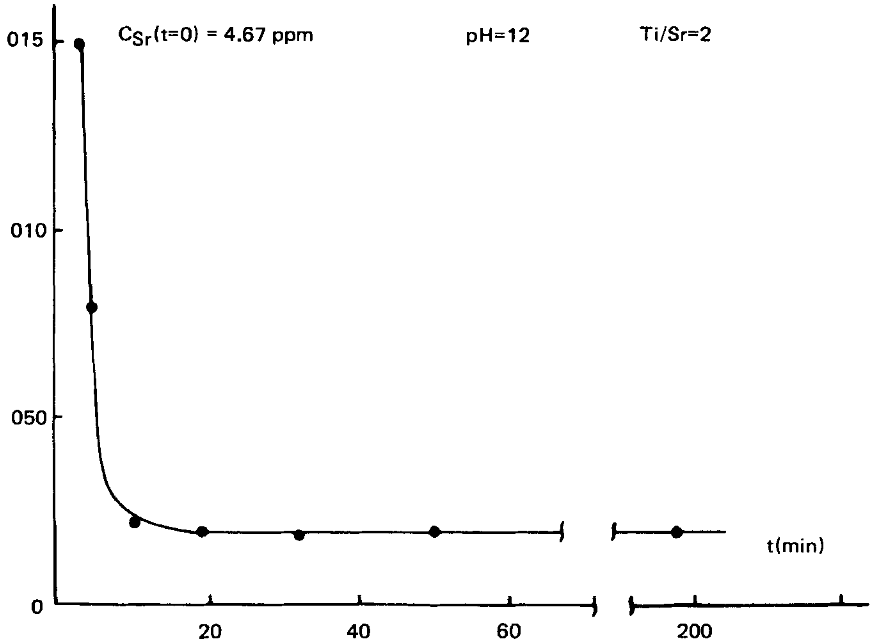

FIG. 3. Adsorption kinetic of Sr on titanium hydroxide colloid particles.

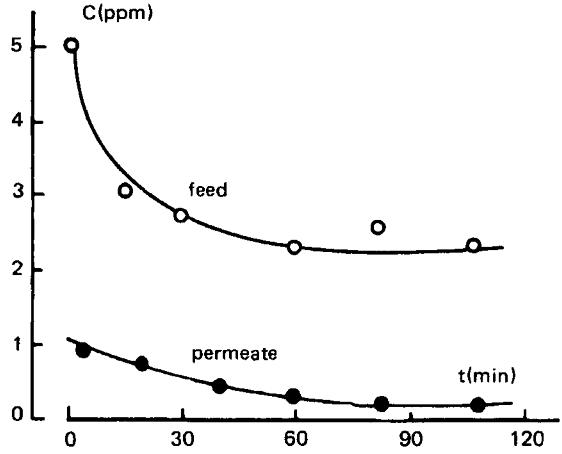

FIG. 4. Time dependence of feed and permeate solutions during a separation test. Sr concentration C (ppm), Ti/Sr = 2, pH = 10.

beginning of the separation. The data of Table 3 represent a typical experiment. From these data it is noticed that almost all the Sr (more than 94% of the feed solution) is confined to the membrane. In fact, it is well known that during the filtration of colloid dispersions, particles stick to the membrane and form a dynamic fouling surface which generally shows two effects. A positive one is the increase in the solute rejection coefficient calculated as $R = (1/C_F)(C_F - C_P)$ (7) where C_F and C_P are the

TABLE 3
Sr-Titanium Hydroxide Colloidal Particles Retention Data on Amicon Hollow Fiber Module H1P5 (feed solution, 2080 cm^3; Sr(NO$_3$)$_2$, 5 ppm; Ti/Sr = 2; pH 10; flow rate, 14 cm^3/min; void volume, 180 cm^3: R index for retentate and P index for permeate)

t (min)	V_R (cm^3)	C_R (ppm)	V_P (cm^3)	C_P (ppm)
0	2080	5.00	—	—
5	1970	5.00	10	0.90
20	1650	3.05	250	0.75
41	1320	2.70	580	0.45
60	1100	2.25	800	0.30
83	680	2.60	1220	0.25
108	100	2.40	1800	0.25

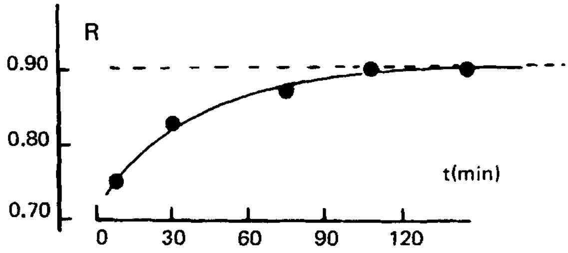

FIG. 5. Rejection coefficient for the experiment of Fig. 4.

feed and permeate Sr concentrations, respectively. As shown in Fig. 5, the rejection reaches a plateau corresponding to a R = 0.9 value. The second effect expected is a decrease in volume permeability. However, this effect was not observed (see Fig. 2), probably because of the reduced duration of the separation test and the small transmembrane pressure used (small compaction of the dynamically formed layer).

Because of the nature of the adsorbing colloid the pH, the titanium concentration, and the presence of other hydrolyzed species should affect the conditions for the separation process.

The effect of the Ti concentration on the separation efficiency was evaluated by changing the Ti/Sr equivalent ratio at a fixed pH (pH 10) and Sr concentration (5 ppm). In Fig. 6 the time evolution of the Sr concentration in the permeate is shown at two Ti/Sr ratio values. The condition Ti/Sr = 2, maintained in the following experiments, was derived from these curves as a compromise between the adsorption

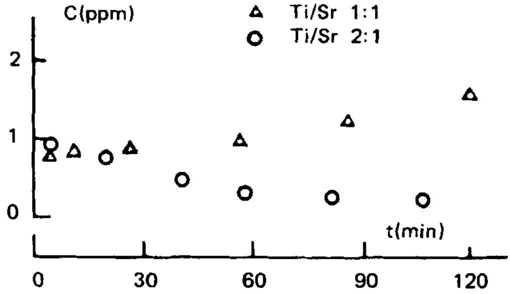

FIG. 6. Sr concentration time dependence in the permeate as a function of the Ti/Sr equivalent ratio, pH = 10.

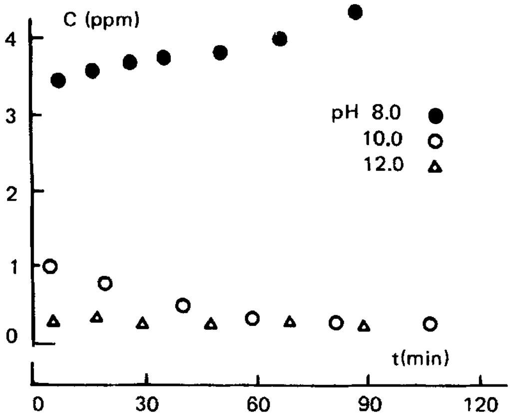

FIG. 7. Sr concentration time dependence in the permeate as a function of pH, Ti/Sr = 2.

capacity and the colloid flocculation. In fact, above the Ti/Sr = 2 value a large precipitation of the colloid was observed which reduces the flow rate of the feed solution in the hollow fiber.

The effect of the pH of the feed solution is shown in Fig. 7. An increase of pH increases the negative surface charge density of the colloid particles available for Sr^{2+} adsorption according to Eq. (1). At pH 8 a small fraction of Sr cations is adsorbed and a small membrane retention is observed. This behavior agrees with the data obtained from batch experiments and reported in Table 2. Therefore, all other experiments were performed in the pH range 10–12 with a fixed Ti/Sr = 2 ratio.

The interaction of alkaline-earth metals has a stronger effect for Sr than for Ca or Mg. However, the interference of competing ions, even when they are poorly adsorbed on colloid particles, can be a critical factor. In fact, this interaction strongly depends on the concentration. As shown in Fig. 8, a 2/1 Mg/Sr ratio leads to practically no retention of Sr on the titanium colloid. This effect may be important when real solutions are processed, for example, S11 solutions, if high concentrations of indifferent electrolytes are present.

Finally, Zr hydroxide has been tested as an alternative adsorbing phase. The main reason for this test is the presence of Zr in the storage pond solution. At moderate metal concentration and pH > 6, the only existing species in Zr solutions is $Zr(OH)_5^-$ according to the equilibrium (*8*)

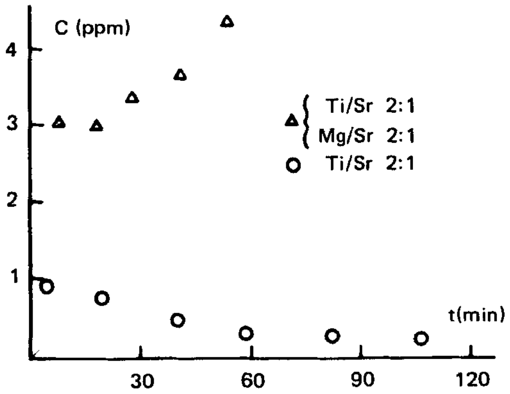

FIG. 8. Effect of Mg as the interfering ion in Sr separation, pH = 10.

$$Zr^{4+} + 5H_2O \rightleftharpoons Zr(OH)_5^- + 5H^+ \qquad (\log K = -16) \qquad (3)$$

The $Zr(OH)_5^-$ colloid particles can adsorb metal cations. The results reported in Fig. 9 show, however, that the Zr colloid, even at a Zr/Sr = 3 equivalent ratio, is not as effective as the Ti colloid in retaining Sr cations.

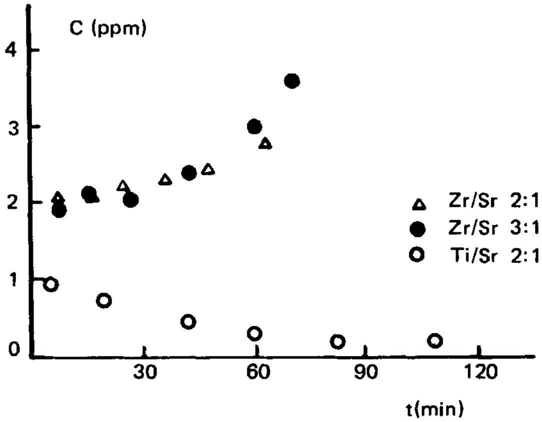

FIG. 9. Colloidal Zr hydroxide as adsorbing particles for Sr separation, pH = 10.

All the results obtained are presented in Table 4 where the hollow fiber membrane performance is characterized by means of a concentration reduction factor CRF = C_F/C_P. Based on these data, the best separation is obtained at Ti/Sr = 2, pH = 10–12 for a volume reduction factor of 20.

Low Activity Solutions

The conditions previously derived were used to process low activity P and S11 solutions. The two sets of experimental results are reported in Tables 5 and 6. In Table 5 a synthetic solution was first considered and a DF close to the CRF coefficient reported in Table 4 was obtained. On the other hand, S11 solutions were not decontaminated, and an increase of the Ti/Sr ratio up to 8 did not improve the results. In Experiment 4 a higher DF was obtained by increasing both the pH (pH 12) and the colloid formation time (15 h vs the 2–3 h of previous experiments). The absence of decontamination for S11 solutions is essentially due to the high $NaNO_3$ concentration. The Na^+ ion saturates the colloid adsorption sites and Sr^{2+} is poorly retained.

The results of Table 6 are directly comparable with the experiments performed with nonactive solutions. In fact, in a water storage pond the electrolyte concentration is not as high as in S11 solutions. If the colloid

TABLE 4
Strontium Concentration Reduction Factor CRF = C_F/C_P (feed concentration C_F = 5 ppm Sr as $Sr(NO_3)_2$; permeate concentration C_P for a volume reduction factor of 20)

Feed (M_1/M_2 equivalent ratio)	Flow rate (cm^3/min)	CRF
Ti/Sr = 2:		
pH = 8	19.5	1.1
10	14.5	20.0
12	18.5	25.0
Ti/Sr = 1		
pH = 10	15.2	3.2
Ti/Sr = 2		
Ti/Mg = 1		
pH = 10	38.0	1.2
Zr/Sr = 2		
pH = 10	29.2	1.8
Zr/Sr = 3		
pH = 3	23.8	1.4

TABLE 5
Decontamination of S11 Solutions (feed volume V_F = 2000 cm^3; prefilter Millipore, 0.45 μm; added carrier Sr, 5 ppm; added ^{85}Sr standard, V = 0.5 cm^3; Sr-titanium hydroxide reaction time, 3 h)

Feed	Ti (ppm)	Ti/Sr (equivalent ratio)	DF
Water	10	2	13.5
S11 solutions:			
1	5	1	1.36
2	10	2	1.14
3	20	4	1.70
4	40	8	4.80, pH = 12, reaction time 12 h

remains in contact with P solutions (under stirring conditions) during 30 h before filtration a high DF is observed. This results and the data of Table 5 show the importance of the colloid formation time and the adsorption kinetic on the separation process. Moreover by using a prefilter with mean pore diameter of 0.2 μm a DF higher than 100 is obtained. However, long contact time between the adsorbing phase and the solution to be decontaminated is a negative condition for real plant operations.

CONCLUSIONS

Strontium metal ions in dilute solutions (~10^{-5} *M*) can be separated from the solution by adsorption on titanium hydroxide colloid particles

TABLE 6
Decontamination of P Solutions (feed volume V_F = 200 cm^3; prefilter Millipore, 0.45 μm; added carrier Sr, 5 ppm; added ^{85}Sr standard, V = 0.05 cm^3)

P solutions	Ti (ppm) (equivalent ratio)	Ti/Sr	Reaction time (h)	DF
1	40	8	15	5.5
2	20	4	15	6.4
3	10	2	15	12.0
4	10	2	30	68.9
5	10	2	15	18.7, Millipore 0.45 μm
6	10	2	30	143.0, Millipore 0.20 μm

and ultrafiltration of the resulting dispersion. The pH of the solution must be fixed in the 10–12 range.

With a Ti/Sr equivalent ratio of 2, the rejection coefficient can be as high as 0.90. However, the presence of interfering ions like Mg can prevent the Sr separation by adsorption-ultrafiltration. This method can not be used in solutions with a high concentration of indifferent electrolyte because of the very low selectivity of titanium hydroxide colloid particles.

The results obtained with P solutions (the storage pond water) show the potential usefulness of the method to control pond radioactivity. In fact, a DF of 147 with a volume reduction factor of 20 are acceptable basis for optimization studies. Moreover the evidence that most of the radioactive colloid is retained by the membrane or the prefilter is an interesting result as solid wastes can be easily handled.

However to have a complete picture for scale-up purposes, long-term tests to study the membrane fouling and characterize the membrane module lifetime are needed.

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